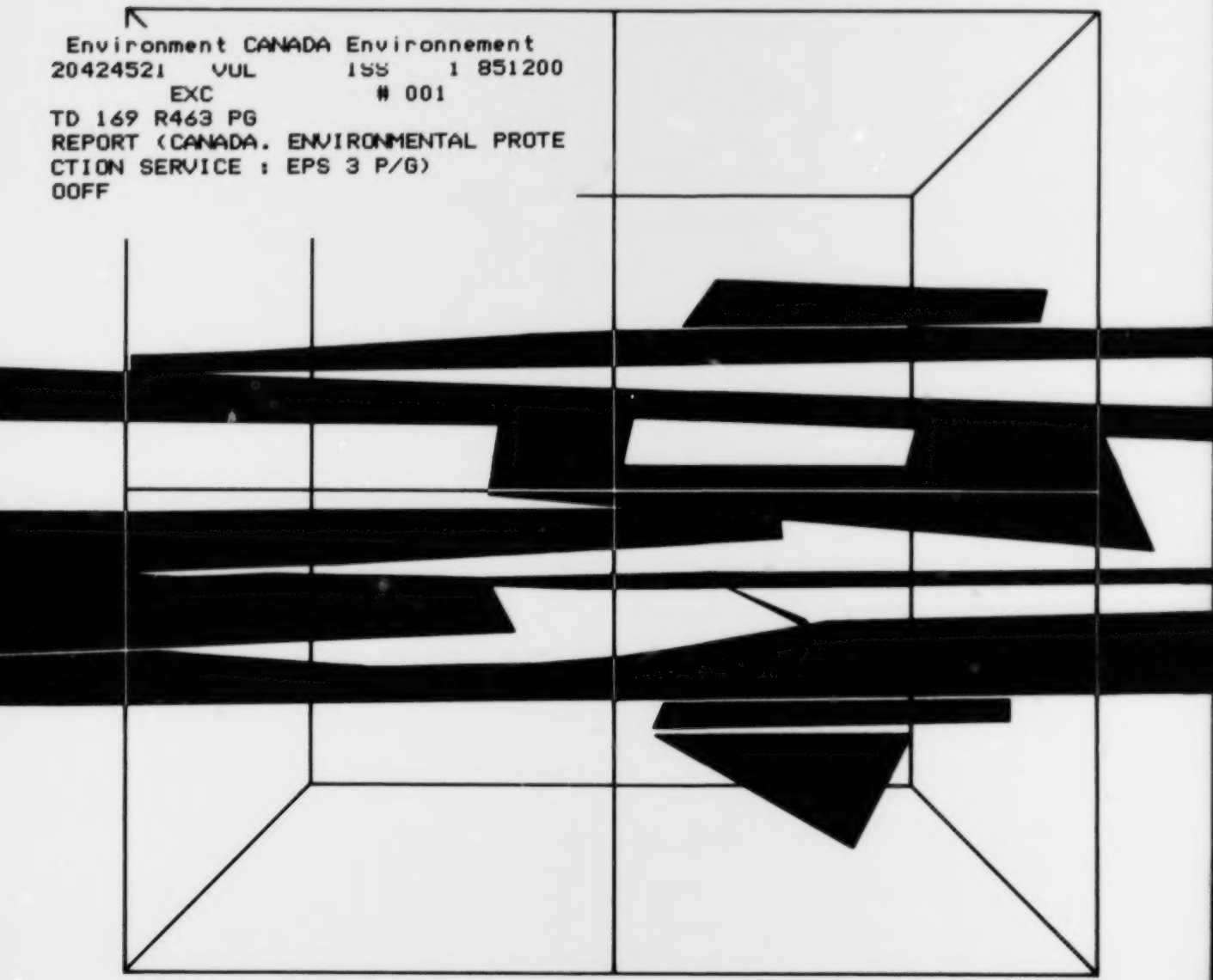
Radioactivity in Coal, Ashes and Selected Wastewaters from Canadian Coal-fired Steam Electric Generating Stations

Report EPS 3/PG/1
September 1985

1885 1985

Environment CANADA Environnement
20424521 VUL 155 1 851200
EXC # 001
TD 169 R463 PG
REPORT (CANADA. ENVIRONMENTAL PROTE
CTION SERVICE : EPS 3 P/G)
OOFF



Environment Canada
Environmental Protection Service

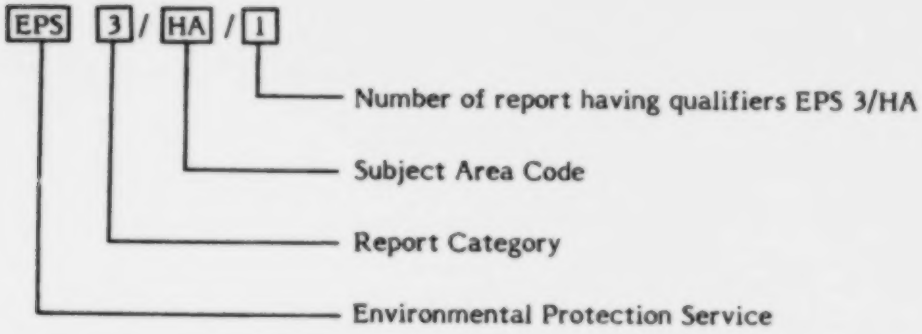
Environnement Canada
Service de la protection de l'environnement

Canada

86-04787/

ENVIRONMENTAL PROTECTION SERVICE REPORT SERIES

Sample Number:



Categories

1	Regulations/Guidelines/Codes of Practice
2	Public Consultation: Problem Assessment, Control Options
3	Research and Technology Development
4	Literature Reviews
5	Surveys
6	Social, Economic and Environmental Impact Assessments
7	Surveillance
8	Policy Proposals & Statements
9	Manuals

Subject Areas

AG	Agriculture
AP	Airborne Pollutants
AT	Aquatic Toxicity
CC	Commercial Chemicals
CP	Consumer Pollution
FP	Food Processing
HA	Hazardous Wastes
IC	Inorganic Chemicals
MA	Marine Pollution
MM	Mining & Mineral Processing
NR	Northern Regions
PF	Paper and Fibres
PG	Power Generation
PN	Petroleum and Natural Gas
SP	Oil & Chemical Spills
SRM	Standard Reference Methods
TS	Transportation Systems
UP	Urban Pollution

New subject areas and codes are introduced as they become necessary. A list of EPS reports may be obtained from the Publications Section, Environmental Protection Service, Environment Canada, Ottawa, Ontario, Canada, K1A 1C8.

National Parks Centennial
1885
1985
Centenaire des parcs nationaux

1885–1985:
100 years of Heritage Conservation
Canada's first national park was established in 1885 at Banff, Alberta. Today there are national parks and national historic parks in every province and territory. The National Parks Centennial is an occasion to renew our commitment to preserve examples of our heritage unimpaired for the benefit of all Canadians.

RADIOACTIVITY IN COAL, ASHES AND SELECTED WASTEWATERS FROM CANADIAN COAL-FIRED STEAM ELECTRIC GENERATING STATIONS

by

Dearborn Environmental Consulting Services

for the
Industrial Programs Branch
Environmental Protection Service
Environment Canada

EPS 3/PG/1
September 1985

© Minister of Supply and Services Canada 1985
Cat. No. En 49-9/3-1E
ISBN 0-662-14234-9
BEAUREGARD PRESS LIMITED

REVIEW NOTICE

This report has been reviewed by the Environmental Protection Programs Directorate, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute recommendation or endorsement for use.

READERS COMMENTS

Readers who wish to comment on the content of this report should address their comments to -

Lawrence A. Dwyer
Industrial Programs Branch
Environmental Protection Service
Environment Canada
Ottawa, Ontario
K1A 1C8

ABSTRACT

Coal is known to contain naturally occurring radioactive elements and there has been speculation that as a result, coal-fuelled power generation stations may be significant emitters of these substances.

In this report, the subject of radioactivity is introduced. The kinds of radioactive substances which occur naturally in coal formations, the nature of their emissions and the existing information on their behaviour and their effects on environmental organisms are also reviewed.

The results of an examination of levels of alpha, beta and gamma radiation levels, and the substances which produce them in coals, fly ashes, bottom ashes and related wastewaters at six Canadian coal-fuelled power stations are presented. Difficulties in studies of this nature and the potential effects of these releases on organisms in the adjacent aquatic environment are discussed. Existing and potential technologies for the removal of these substances from wastewaters are examined.

In general the releases in wastewaters from the six stations were found to be lower than those known to cause short-term or acute biological effects. The potential for long-term effects from such low-level releases could not be accurately assessed because of the paucity of information.

A number of recommendations for: improvements in further studies of this nature; the further examination of the fate of naturally occurring radionuclides in the environment; and the determination of the long-term effects of low levels of naturally occurring radioactive substances on aquatic organisms, are made.

RÉSUMÉ

Comme le charbon est réputé contenir des radioéléments naturels, on s'est demandé si les centrales électriques à charbon pouvaient en émettre notablement.

Dans le rapport, la notion de radioactivité est présentée, de même que sont exposés la nature des radioéléments trouvés naturellement dans les formations houillères, celle de leurs émissions et ce qu'on sait de leur comportement et de leurs effets biologiques.

On communique les résultats de l'examen de l'intensité du rayonnement α, β et γ des substances qui en sont à l'origine, dans le charbon, les cendres volantes, les cendres du cendrier et les eaux résiduaires de six centrales canadiennes à charbon. On discute des difficultés d'étudier la nature et les effets potentiels de ces rejets sur les organismes des milieux aquatiques contigus. On examine les techniques actuelles et possibles d'épuration des eaux résiduaires de ces substances.

En général, les quantités trouvées dans les eaux résiduaires des six centrales se sont révélées inférieures à celles qui ont des effets biologiques aigus ou à court terme avérés. La possibilité d'effets à long terme n'a pas pu être estimée correctement, à cause de la rareté des informations.

On fait un certain nombre de recommandations pour améliorer les études ultérieures de cette nature, pour examiner le devenir des radionucléides naturels dans l'environnement et pour déterminer les effets à long terme des faibles concentrations de radioéléments naturels sur les organismes aquatiques.

TABLE OF CONTENTS

		Page
ABSTRACT		iii
RÉSUMÉ		iv
LIST OF FIGURES		vii
LIST OF TABLES		viii
ACKNOWLEDGEMENTS		x
1	INTRODUCTION	1
1.1	Objectives	2
1.2	Introduction to Terms and Concepts	2
2	EFFECTS AND SOURCES OF NATURAL RADIONUCLIDES	12
2.1	Environmental Effects of Uranium and Thorium on Aquatic Ecosystems	12
2.2	Bioaccumulation of Radionuclides	23
2.2.1	Mechanism of Bioaccumulation	25
2.2.2	Factors Affecting Bioaccumulation	26
2.2.3	Effects of Radionuclides within Organisms	30
2.2.4	Facting Affecting Radiotoxicity of Radionuclides	31
2.2.5	Examples of Radiotoxicity	32
2.2.6	Aquatic Systems	34
2.2.7	Terrestrial Systems	35
2.2.8	Bioaccumulation Near Coal-fired Power Plants	35
2.3	Radioactivity in Coals, Ashes and Wastewater from Coal-fired Generating Stations	39
2.3.1	Radionuclides in Coal	39
2.3.2	Radioactive Releases Prior to Coal Combustion	45
2.3.3	Radioactive Releases During Coal Combustion	49
2.3.4	Radionuclide Releases Resulting From the Solid Wastes of Coal Combustion	53
2.4	Summary	57
3	SAMPLING PROGRAM AND ANALYTICAL METHODS	59
3.1	Sampling Program	59
3.2	Analytical Procedures	63
4	ANALYTICAL RESULTS	68
4.1	Coal Pile Runoff	72
4.2	Coal	79
4.3	Ash System Overflow	80
4.4	Concentration Factors	84

		Page
4.5	Comparison of Analytical Techniques	84
4.6	Summary	86
5	REMOVAL OF RADIONUCLIDES FROM COAL COMBUSTION WASTEWATERS	88
5.1	Introduction	88
5.2	Treatability of Coal Combustion Wastewaters	89
5.2.1	Conventional Treatment	89
5.2.2	Biological Methods	90
5.2.3	Physical - Chemical Methods	91
CONCLUSIONS AND RECOMMENDATIONS		94
REFERENCES		99
APPENDIX		111

LIST OF FIGURES

Figure		Page
1	ABILITY OF VARIOUS SHIELDS TO STOP ALPHA, BETA AND GAMMA RADIATION	6
2	EFFECTS OF GAMMA RADIATION	7
3	URANIUM - 238 DECAY SERIES	10
4	THORIUM - 232 DECAY SERIES	11
5	STEADY-STATE DISTRIBUTION OF RADIONUCLIDES IN AN AQUATIC SYSTEM	24
6	NORMAL METABOLIC FUNCTIONING FOR A MACRONUTRIENT (Sodium) AND A MICRONUTRIENT (Selenium)	27
7	RADIONUCLIDE CONCENTRATION vs COAL RANK (U.S. Coals)	43
8	RADIONUCLIDE CONCENTRATION vs COAL RANK (Canadian Coals)	46
9	PROCESSES WITHIN A GENERATING STATION	69
10	TEMPORAL VARIATION IN COAL PILE RUNOFF	78

LIST OF TABLES

Table		Page
1	THE SPECIFIC ACTIVITIES OF SOME MEMBERS OF THE URANIUM AND THORIUM SERIES	9
2	URANIUM CONCENTRATIONS IN VARIOUS NATURAL WATERS	15
3	URANIUM CONCENTRATIONS OF ORGANISMS IN A FLY ASH POND AND A CONTROL POND AT THE MILLIKEN ELECTRIC POWER GENERATING PLANT, LANSING, NEW YORK	18
4	TOXICITY OF URANIUM COMPOUNDS TO FISH	20
5	THORIUM CONCENTRATIONS OF ORGANISMS IN A FLY ASH AND CONTROL POND AT THE MILLIKEN ELECTRIC POWER GENERATING PLANT, LANSING, NEW YORK	22
6	CONCENTRATIONS AND ACTIVITIES OF ^{238}U, ^{232}TH and ^{40}K IN U.S. COALS	40
7	AVERAGE CONCENTRATIONS AND ACTIVITIES OF RADIONUCLIDES IN U.S. COALS	41
8	CONCENTRATIONS AND ACTIVITIES OF ^{238}U, ^{232}TH, and ^{40}K IN CANADIAN COALS	44
9	RADIONUCLIDES IN COAL PILE DRAINAGE	47
10	^{222} Rn EMANATION FROM COAL PILES AND SOILS	48
11	CONCENTRATIONS OF PRIMORDIAL RADIONUCLIDES IN POST-ESP FLY ASH	50
12	ACTIVITIES OF RADIONUCLIDES IN ESCAPING FLY ASH	50
13	ESTIMATES OF ANNUAL RADIONUCLIDE RELEASES FROM 1000 MW (e) U.S. COAL-FIRED POWER PLANTS	52
14	ESTIMATES OF ANNUAL RADIONUCLIDE RELEASES CANADIAN COAL-FIRED POWER PLANTS	54
15	RADIOACTIVITY IN ASH SAMPLES COLLECTED IN POWER PLANTS IN THE UNITED STATES	55
16	RADIONUCLIDES LEACHED FROM FLY ASH	56
17	RADIOACTIVITY IN ASH FROM THE NANTICOKE GENERATING STATION	56

Table		Page
18	CHARACTERISTICS OF STATIONS SAMPLED DURING THE FIELD PROGRAM	60
19	SUMMARY OF SAMPLING PROGRAM	61
20	URANIUM SERIES AND THORIUM SERIES ISOTOPES MEASURED BY GAMMA SPECTROSCOPY	67
21	RADIONUCLIDE BALANCE FOR TRENTON GENERATING STATION	69
22	RADIONUCLIDE BALANCE FOR DALHOUSIE GENERATING STATION	70
23	RADIONUCLIDE BALANCE FOR LAMBTON GENERATING STATION	71
24	RADIONUCLIDE BALANCE FOR BOUNDARY DAM GENERATING STATION	72
25	RADIONUCLIDE BALANCE FOR SUNDANCE GENERATING STATION	73
26	RADIONUCLIDE BALANCE FOR MILNER GENERATING STATION	74
27	CHEMICAL CHARACTERISTICS OF COAL PILE DRAINAGE	75
28	CHEMICAL AND RADIOCHEMICAL COMPOSITION OF COAL PILE RUNOFF SAMPLES	76
29	COAL RANK AND RADIONUCLIDE CONCENTRATIONS	80
30	RADIONUCLIDE CONCENTRATION IN FLY ASH, BOTTOM ASH AND PYRITES FROM DALHOUSIE GENERATING STATION	81
31	CHEMICAL CHARACTERISTICS OF ASH SYSTEM OVERFLOWS	82
32	CHEMICAL AND RADIOCHEMICAL COMPOSITION OF ASH SYSTEM OVERFLOW SAMPLES	83
33	CONCENTRATION FACTORS FOR URANIUM AND THORIUM	85
34	COMPARISON OF URANIUM RESULTS FROM TRENTON GENERATING STATION AS DETERMINED BY NAA AND GAMMA SPECTROSCOPY	85

ACKNOWLEDGEMENTS

This study was conducted by R. Kissel of Dearborn Environmental Consulting Services with the assistance of Dr. G. Smithson, Head, Analytical Laboratory and Dr. S. Swanson, Research Scientist, Environmental Studies Section, of the Saskatchewan Research Council and Mrs. E. Sheridan, Consulting Biologist. The scientific authority for the project was Mr. L.A. Dwyer, Program Officer, Oil Gas and Energy Division, Industrial Programs Branch, Environment Canada.

We wish to acknowledge the assistance of the following individuals during the project:

Nova Scotia Power Corporation

Mr. P. LeBlanc, Senior Advisor - Environment

Mr. O. Betancourt, Senior Environmental Engineer, Thermal Production Division

Mr. C.A. Pearce, Operations Superintendent, Trenton G.S.

New Brunswick Electric Power Commission

Mr. C.C. Doiron, Supervisor, Environmental and Chemical Operation

Mr. J.M. Legere, Area Chemical Controls Supervisor, Dalhousie G.S.

Ontario Hydro

Dr. A.W. Jackson, Technical Supervisor, Environmental Protection Department, Thermal Generation Services

Mr. P. Hicks, Chemical, Fuels and Environment Superintendent, Lambton G.S.

Saskatchewan Power Corporation

Mr. W.H. Gardiner, Chief Chemist, Power Supply Engineering

Mr. B. Baker, Station Chemist, Boundary Dam G.S.

Alberta Power Limited

Mr. W. Symington, Energy Supply

Mr. R. Thonitt, Plant Manager, Milner G.S.

TransAlta Utilities Corporation

Mr. G.D. Bateson, Chemical Engineer

1 INTRODUCTION

The contamination of waters by coal-based energy technologies, including coal-fired steam electric generating stations, has recently been the subject of much investigation. To date, emphasis has been placed on the physical, biological and chemical characteristics of the contaminants. There has also been speculation concerning the radioactive emissions from coal-fuelled steam electric power generating stations. Unfortunately, there is at present very little information about the activities of the natural decay radionuclides around the stations and in releases to the environment.

The levels and types of radioactive contaminants in coal may vary considerably from deposit to deposit. The pathways through the station and levels of release are, in part, dependent on site-specific factors such as station design and coal fuel. These factors must be taken into consideration when making comparisons between different sites.

To date, the focus on the hazards of radioactive releases from power generation has mainly concerned releases from nuclear-fuelled stations and the eventual effects of these substances if ingested by humans after dilution in the environment's receiving waters. Actual levels of release before dilution have not been emphasized and the possible effects on the exposed aquatic and terrestrial wildlife communities have not been considered directly.

Canadian environmental protection guidelines for trace contaminant releases from coal-fuelled stations are based on the best practicable control of contaminant levels before release or dilution and on the protection of organisms in the adjacent environment. In order to examine the need for such guidelines, documentation of the actual levels of contamination and an assessment of the impact of radioactive wastewaters on organisms in the adjacent environment is required.

The focus of this study was the determination of actual levels of radioactivity and their sources from coal piles through the station systems to discharges into the receiving water. The individual radioactive substances and the manner in which they partition between the solid and liquid waste streams were also examined in order to examine appropriate protection technologies and procedures.

1.1 Objectives

The overall objective of this study was to investigate the radioactivity in coals, ashes and related wastewater streams at Canadian steam electric generating stations. The detailed objectives of the program were:

- To review and summarize the literature on radioactivity and radioactive substances in coals, ashes, and related wastewaters at coal-fuelled, power generating stations as well as the potential toxic effects on environmental organisms and the ability of current practicable wastewater treatment technologies to remove them before dilution or discharge.
- To examine the levels of alpha, beta, and gamma radiation in coals, fly and bottom ashes and related wastewaters at six representative Canadian coal-fuelled steam electric power generating stations across the country and wherever possible, identify and quantify the specific radionuclides involved.
- To determine the gross water quality characteristics such as pH, TDS and TSS of the potentially contaminated wastewaters and, if possible, relate these to degree of measured contamination.
- To estimate partitioning of the radioactivity in the bottom and fly ashes and a concentration factor from coal to ashes.
- To assess the direct impacts of radioactive discharges on the organisms in the adjacent environment.
- To discuss practicable wastewater treatments and/or other environmental protection measures which may be utilized to reduce radioactive discharges.

1.2 Introduction to Terms and Concepts

The Scientific Basis of Radioactivity. The study of radioactivity in the environment requires an understanding of two levels of science: atomic and nuclear. Atomic (or molecular) relates to chemical processes involving the electrons in orbit about the nuclei of the atoms; nuclear relates to the high energy processes involving components of the nucleus of the atom. Chemistry deals with the interaction of atoms or molecules and provides information on their behaviour which, for example, would be useful in the treatment of radioactive waste streams. Nuclear physics, on the other hand, describes properties of the nucleus and explains the processes of radioactivity, radioactive decay and the behaviour of radiation. To fully understand the environmental effects of

radioactivity, therefore, both the atomic or chemical and nuclear or radioactive aspects of the substances must be considered.

Isotopes. Each chemical element is made up of several types of similar atoms called isotopes. An isotope is a species of an atom with the same atomic number (number of protons) but a different mass number (number of protons plus neutrons). For example, stable ^{206} lead (^{206}Pb) and radioactive ^{210} lead are both isotopes of the element lead.

Many of the isotopes in nature are stable and remain unchanged through all chemical processes. This occurs since it is the electrons that are involved in the chemical processes. For the stable elements, the normal number of neutrons present in the nucleus is equal to or slightly greater than the number of protons. When the number of neutrons is less than or larger than this stable complement, however, the nucleus is unstable and the isotope is called a radioisotope. A radioisotope spontaneously disintegrates or "decays" in order to achieve a more stable neutron/proton ratio, as well as to decrease the size of its nucleus to that of an element which is stable. The decay process cannot be accelerated or retarded by chemical interactions, and the radioactivity cannot be destroyed by chemical means.

Half-life and Activity. The number of radioactive atoms that decay at any moment of time depends on two things:

- the number of atoms, and
- the nuclear species (the particular isotope).

Each isotope has its own half-life ($t_{0.5}$), which is the length of time required for half of the original amount of its atoms to decay. For example, the $t_{0.5}$ for ^{210}Pb is 22.3 years; if there are 1000 atoms of ^{210}Pb now, after 22.3 years there would be 500 atoms, and after 44.6 years, 250 atoms, and so on.

The rate of decay or number of disintegrations of nuclei per second (d/s) is called the activity. The unit of becquerel (Bq) refers to the activity of one d/s. Activity decreases with time in the same way as the number of atoms decreases with time. Consequently, the smaller the amount of the radionuclide present and the longer its half-life, the smaller is the activity.

Radioactive decay is a first order reaction; with the rate of decay being proportional to the amount of concentration of the isotope raised to the first power:

rate = constant x concentration

or, $$\frac{dN}{dt} = -\lambda N$$

Where: N is the number of atoms present
t is the elapsed time
λ is the decay constant

Integration of this first order equation yields:

$$N = Noe^{-\lambda t}$$

Where: N is the number of atoms at time 't'
N_o is the number of atoms initially present

Substituting 0.5 for N/N_o and solving the equation leaves:

$$t_{0.5} = \frac{\ln 2}{\lambda}$$

The rate constant and the half-life are unique for each radionuclide.

Kinds of Radioactive Emission. The process by which radioisotopes change their nuclear structure in the direction of a stable configuration include alpha decay, beta decay and/or electron capture, and gamma decay. Alpha decay (α) is the process whereby an atom with an unstable nucleus reduces its mass towards a smaller, stable mass. Ejection of the alpha particle (a helium nucleus) which is composed of two protons and two neutrons, results in a decrease in both the mass number (4 units) and the atomic number (2 units) of the isotope. For example:

$$\underset{88}{^{226}Ra} \rightarrow \underset{86}{^{222}Ra} + \underset{2}{^{4}He\ (\alpha)}$$

The beta particle is a high velocity negative electron. Beta decay (β) occurs with radioisotopes whose neutron/proton ratio is too high for stability. This produces either normal beta decay in which a neutron becomes a proton by emitting an electron (e), or electron capture in which one of the orbiting electrons is pulled into the nucleus and combines with a proton to form a neutron. Both these processes result in the mass of the nucleus remaining unchanged, but its atomic number being increased by one:

$$\underset{90}{^{234}Th} \rightarrow \underset{91}{^{234}Pa} + \underset{-1}{^{0}e}$$

The third main type of radioactive emission is electromagnetic radiation. Bohr's theory explains that electrons that "jump" into an orbit of larger radius absorb energy, while those that "jump" into a smaller orbit emit energy. Gamma emission, one form of electromagnetic radiation, is the process by which an atom's residual excess

energy is emitted after having undergone alpha or beta decay. Although gamma emission often accompanies alpha or beta decay, this is not always the case. Gamma rays are at the high energy end of the electromagnetic spectrum. The electromagnetic spectrum includes radio, microwaves, infrared, visible light, ultraviolet, x-rays, and gamma rays in increasing order of energy content.

The Nature of Radioactive Emanations and Methods of Absorption. Radiation from a radioactive source emanates in all directions, similar to visible light from a light bulb. The magnitude of energy released in the alpha, beta or gamma emission influences its ability to penetrate organisms and cause radiation damage. Ingestion and inhalation are two other pathways that alpha radiation and beta radiation may enter organisms. As shown in Figure 1, alpha and beta particle, and gamma ray penetration may be prevented by material barriers. Each type of radiation is slowed down or stopped by collisions with atoms. A sheet of paper is able to stop alpha particles, but it would take a sheet of aluminum metal approximately 1 mm thick to stop high energy beta particles. Lower energy beta particles could be stopped by a thinner aluminum plate. These particles are said to have a certain "range of penetration" which increases with particle energy. Gamma radiation is highly penetrating, making it the most difficult external hazard of the three types of radiation to shield against.

To understand how radiation interacts with matter on a sub-microscopic level, the effects of a collision between a gamma ray and a simple atom may be visualized as shown in Figure 2. The three possible events shown are:

a) scattering, in which the gamma ray bounces off the electron,
b) ionization, in which the energy of the gamma ray goes into removing the electron from the atom, leaving an ion, and
c) pair production in which the gamma ray energy is converted into the mass of two particles - an electron and a positron (positively charged electron).

Natural Radioactivity. Many radioisotopes occur naturally in the earth's atmosphere and crust. These can arise from cosmogenic (bombardment from space) or primordial (in the earth from the beginning) sources. Man-made radioisotopes are also now present as a result of induced fission reactions. Each of these sources produce radioactivity of different energies. In some cases comparisons can be made between these different radioactive substances and their biological effects. In other cases, the induced fission products or "activation" products are unique and indicate man-induced origins.

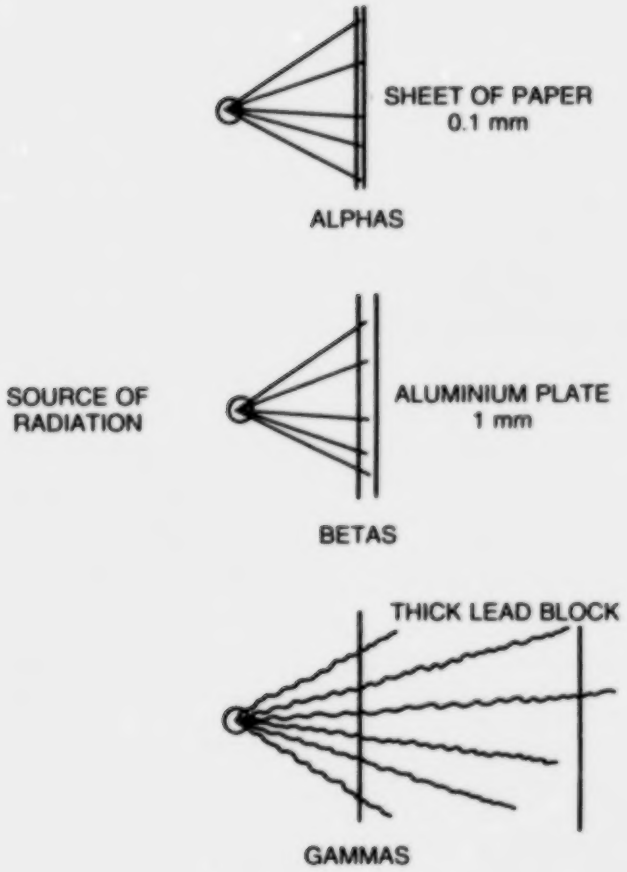


FIGURE 1 ABILITY OF VARIOUS SHIELDS TO STOP ALPHA, BETA AND GAMMA RADIATION (Murray, 1982)

Above the atomic number 80 there are 45 naturally occurring radioisotopes, of which only three have half-lives comparable to the age of the earth. The remainder are members in the decay chains headed by these three long-lived isotopes. In this report emphasis has been placed on the natural uranium, thorium, and actinium decay series, headed by the primordial radionuclides ^{238}U, ^{232}Th and ^{235}U. The latter is commonly associated with the ^{238}U series because ^{235}U typically constitutes 0.71 percent of natural uranium. At this concentration, the activity of ^{235}U is about 4.6 percent that of ^{238}U. It is not usually quantified specifically, as the ^{238}U concentration will allow its concentration to be calculated.

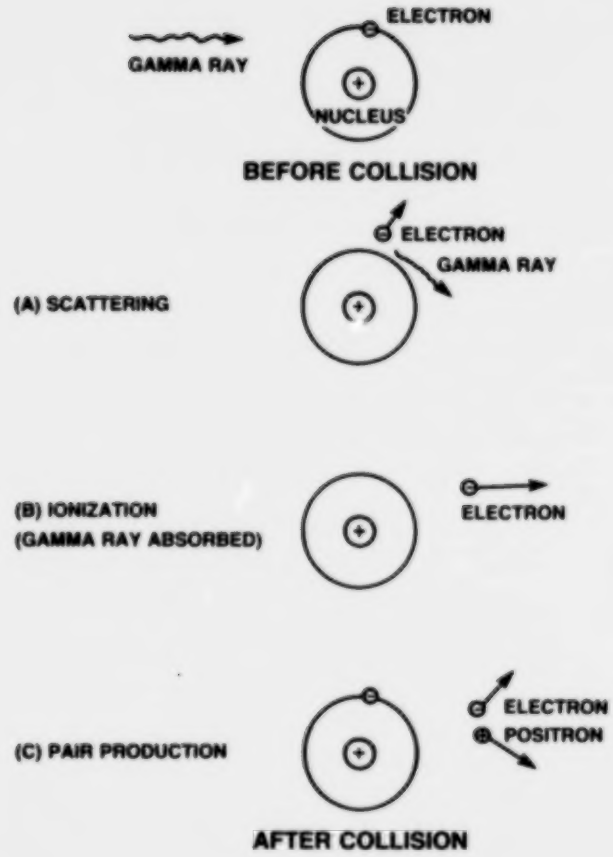


FIGURE 2 EFFECTS OF GAMMA RADIATION (Murray, 1982)

The term 'parent' refers to a radionuclide which decays to form another nuclide (stable or radioactive); and 'daughter' refers to a nuclide which has been produced by the decay of a radionuclide yet has different properties than those of the parent. After 10 half-lives of the longest lived radionuclide in a decay series, all the members of the series will be within 0.1 percent of their final equilibrium. This is known as secular equilibrium during which time all intermediate members are decaying at the same rate as they are being formed.

Although the activity (d/s) is equal for all daughters in a series which is at secular equilibrium, the number of atoms of each daughter is proportional to its half-life. The activity for a given mass of a particular radionuclide, however, is termed "specific activity", which is calculated as: $\frac{A}{M} = \lambda N$

Where: A = specific activity in Bq/g

N = Avogadro's number (6.023×10^{23} atoms/g-atom)

M = atomic weight (g/g-atom)

λ = decay constant (s^{-1})

Using this equation the specific activities have been calculated for some of the members of the uranium and thorium series as shown in Table 1. ^{238}Uranium ^{235}uranium, and ^{232}thorium have extremely long half-lives, in the order of millions of years, making their specific activities very low. These radionuclides may pose a hazard by their chemical toxicity as well as by their radiation effects. On the other hand, a radionuclide with an extremely short half-life may not last long enough to be a chemical biological hazard unless it is being replenished by a parent or is decaying to a daughter with a longer half-life. In this case, it is the parent or the daughter that is usually considered the main hazard. It is primarily those radionuclides with half-lives greater than a few years and less than a million years, therefore, that are generally considered to be the major radiation hazard when discharged into the environment.

Behaviour of Select Radionuclides. The natural uranium decay series, including the half-life ($t_{0.5}$) of each member, the type(s) of radiation emitted, and the principal decay energies are shown in Figure 3. In the ^{238}U series there are four radionuclides with half-lives between one and one million years: ^{234}U, ^{230}Th, ^{226}Ra and ^{210}Pb. Because ^{234}U ($t_{0.5}$ of 250 000 years) and ^{238}U are isotopic, they are not normally separated in monitoring. Monitoring for ^{238}U also allows the upper level of ^{234}U to be calculated on the assumption that ^{235}U is a certain percentage of the total uranium present.

The second radionuclide of concern in this series is ^{230}Th; with a half-life of 80 000 years and a specific activity of 7.2×10^{8} Bq/g it could be a potential hazard if allowed to accumulate in biological systems. Due to its long half-life it acts as a source of ^{226} radium for several hundred thousand years.

^{226}Radium is an important naturally occurring radionuclide because it has a half-life of 1600 years. It is also the parent of ^{222}radon, an inert gas, which has a short half-life of 3.8 days. Since ^{222}Rn can escape into the atmosphere, and it is reasonably soluble in water, it represents an important potential disequilibrium point for loss of secular equilibrium in the decay series.

^{210}Lead, with a half-life of 21 years and a high specific activity, is reasonably mobile in aquatic systems. Its potential hazard as an external radiation source is reduced

TABLE 1 THE SPECIFIC ACTIVITIES OF SOME MEMBERS OF THE URANIUM AND THORIUM SERIES (Smithson, 1980)

Uranium Series	Specific Activities (Bq/g)
^{238}U	1.23×10^{4}
^{234}Th	8.58×10^{14}
^{234}U	2.26×10^{8}
^{230}Th	7.18×10^{8}
^{226}Ra	3.36×10^{10}
^{222}Rn	5.70×10^{15}
^{210}Pb	3.00×10^{12}
^{210}Bi	4.59×10^{15}
^{210}Po	1.66×10^{14}
Thorium Series	
^{232}Th	4.03×10^{3}
^{228}Ra	1.00×10^{13}
^{228}Th	3.03×10^{13}
^{224}Ra	5.96×10^{15}
^{220}Rn	3.46×10^{20}

considerably because it is a weak beta emitter. It eventually decays to ^{210}Po which is an active alpha emitter, therefore, there is a hazard of increase if ^{210}Pb is retained internally.

The thorium decay series, in which the radionuclides generally considered to be most environmentally dangerous, ^{232}Th, ^{228}Th, and ^{228}Ra are included is shown in Figure 4. ^{228}Radium has a half-life of 5.8 years and like ^{210}lead, emits beta particles and decays to a very active alpha emitter, ^{228}Th. ^{228}Thorium has a fairly short half-life of 1.91 years and produces a series of daughters which reach equilibrium in a few weeks. These daughters produce a five-fold increase in the original alpha activity of the ^{228}Th parent. Of the naturally occurring radionuclides with longer half-lifes, ^{228}Th is one of the most intense sources of alpha emission.

Potassium, which has an atomic number of 19 and is not a member of the ^{238}U or ^{232}Th decay series is composed of three isotopes. One of these is ^{40}potassium which has a half-life of 1.3×10^{9} years. It is often included in the study of naturally occurring

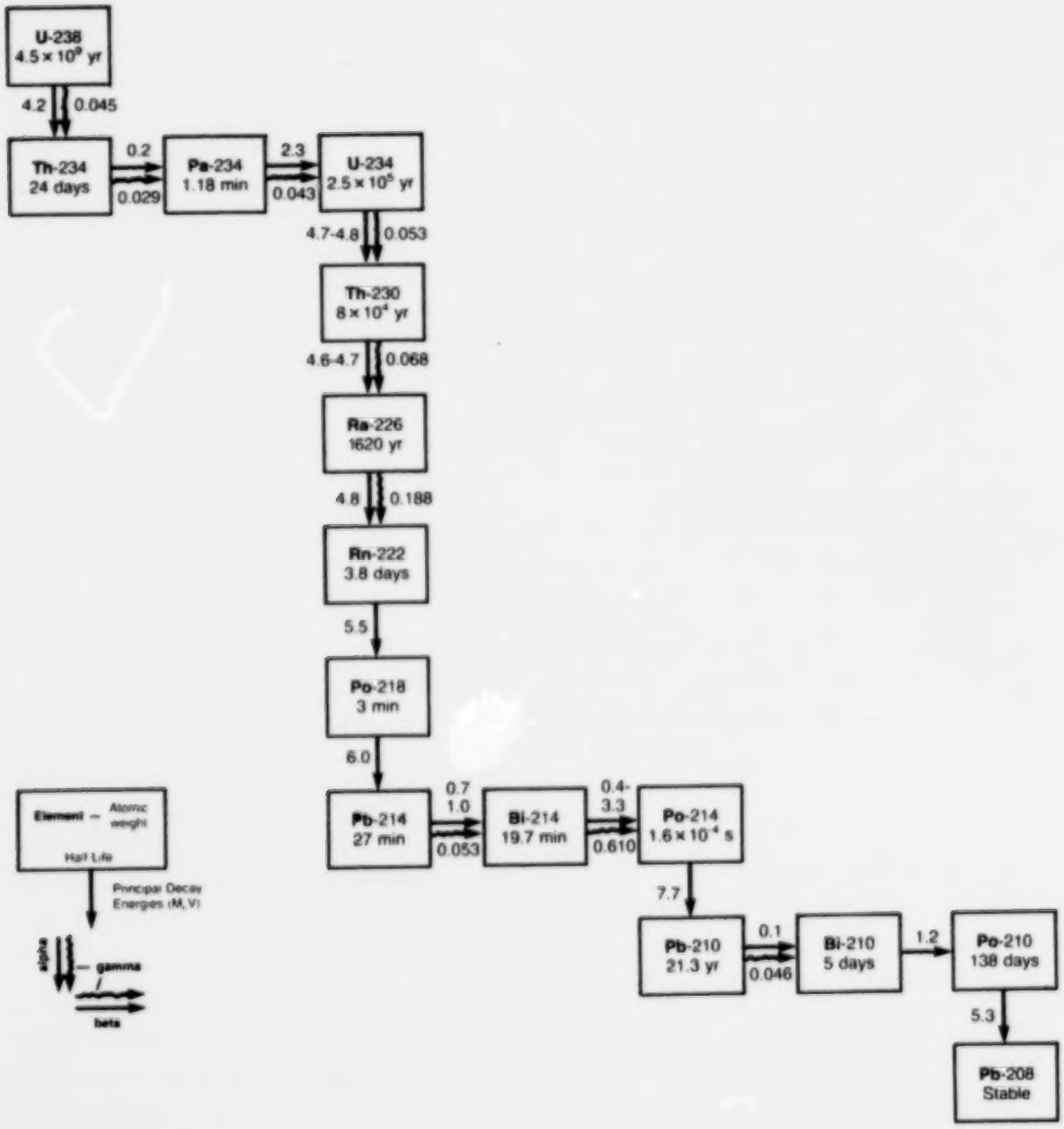


FIGURE 3 URANIUM - 238 DECAY SERIES (Smithson, 1980)

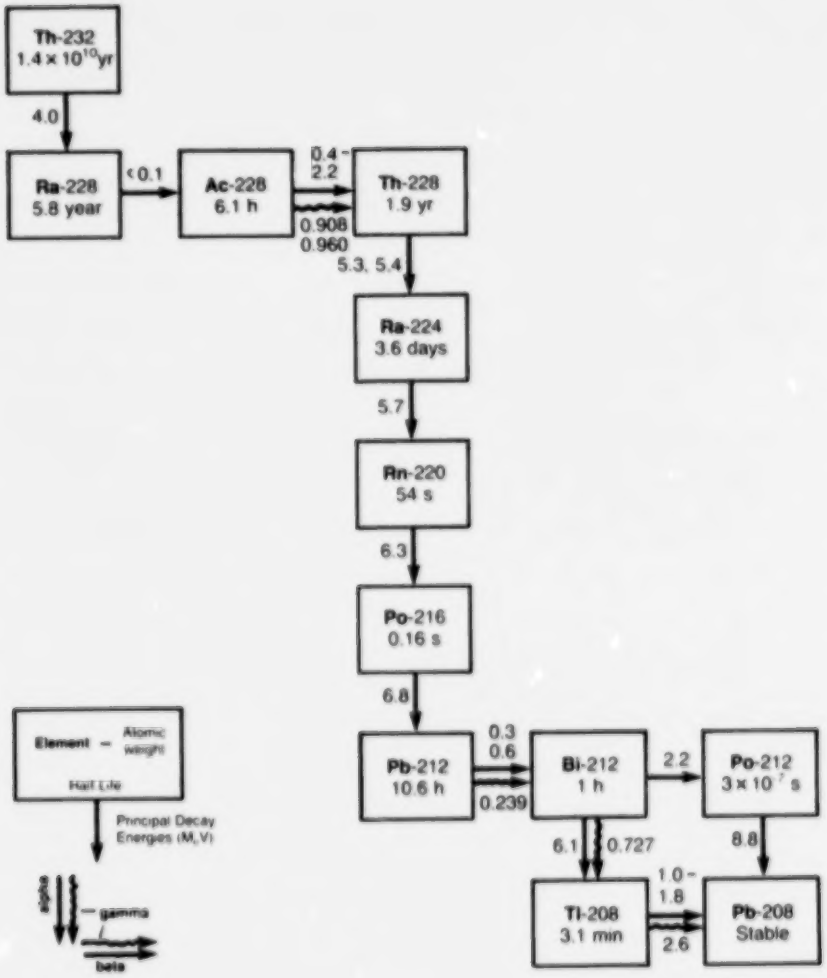


FIGURE 4 THORIUM - 232 DECAY SERIES (Bates et al., 1980)

radionuclides due to its relative abundance and its beta emissions, and because it is the predominant radioactive component in normal foods and human tissues. Since potassium is relatively abundant in coal, it is also included in discussions for purposes of calculations and comparison in this report.

2 EFFECTS AND SOURCES OF NATURAL RADIONUCLIDES

This section of the report contains a review of the literature on the environmental effects and bioaccumulation of uranium and thorium in the aquatic environment. The results of other studies on the radioactive releases from coal, particularly during coal combustion at steam electric generating stations, are also presented.

2.1 Environmental Effects of Uranium and Thorium on Aquatic Ecosystems

Uranium. Uranium has fourteen isotopes, all of which are radioactive (Holm and Persson, 1978; Weast and Astle, 1978; Sheppard, 1980). Natural uranium contains 99.28 percent by weight ^{238}U, 0.71 percent ^{235}U, and 0.01 percent ^{234}U. These isotopes have half-lives of 4.47×10^9, 7.04×10^8, and 2.4×10^5 years, respectively, and all decay primarily by alpha emission (Till et al., 1976) (Figure 3).

Although uranium is one of the best known elements in the periodic table, its ecological behaviour in the aquatic environment has been poorly documented (Till et al., 1976; Hanson, 1974; Essington et al., 1976). It appears that the environmental importance of uranium has been assessed mainly as a function of its chemotoxicity (Eisenbud and Petrow, 1964; Bates et al., 1980). This has then been taken into consideration in determining maximum permissible concentrations. For example, ^{238}U and ^{235}U are primarily considered as chemical toxicants rather than radiation hazards because of their very long radioactive half-lives and very low specific activities (Justyn and Lusk, 1976). Consequently, any observed uranium effect on aquatic biota has been generally related to short-term chemical toxicity rather than longer radiation or chronic chemical toxicity effect (Till et al., 1976; Hanson, 1974; Gus'kova et al., 1966).

On the other hand, radiobiological effects have been used to determine the maximum permissible concentration values for the shorter-lived uranium isotopes such as ^{230}U, ^{232}U, ^{233}U, ^{234}U, ^{235}U, and ^{240}U. Till et al., (1976) considered ^{233}U to have moderate radiotoxicity, whereas ^{232}U has been characterized by very high radiotoxicity. Since ^{238}U is the predominant naturally occurring uranium isotope, further discussion will focus primarily on this isotope, unless otherwise stated.

Uranium exists in four valence states: U^{3+}, U^{4+}, U^{5+}, and U^{6+} (Sheppard, 1980). In natural waters, the chemical properties of uranium favour hexavalent uranium which often associates with oxygen to form the stable divalent uranyl ion (UO_2^{2+}) (Till et al., 1976). Uranyl salts are soluble in water and readily form soluble ion complexes as

long as the water has a high redox potential (Till et al., 1976; Hanson, 1978; Anon., 1983; Panson and Charles, 1977). Uranium is also commonly found as the tetravalent uranous ion (U^{4+}) in a reducing environment in which form it has a high affinity for organic material. Koczy (1963) reported that the most spectacular uranium increases occur in the reducing environments of the oceans. Uranium can, however, be easily held in solution as the complex uranium tetracarbonate in high carbonate waters (Hanson, 1978). Uranium has generally shown a constant distribution in the water column and a low affinity to water borne particulates (Hanson, 1978). Tannenbaum and Silverston (1951) reported the following chemical toxicities for various uranium compounds:

Compound	Toxicity
UO_2,U_3O_8, UF_4	- relatively nontoxic, even in large doses
UO_3, UCl_4	- toxic in large doses
$UO_2(NO_3)_2$, UO_4, $Na_2U_2O_7$	- toxic in moderate doses
UO_2F_2	- toxic even in relatively small doses, probably due to F toxicity

Uranium in water has been introduced partly from the bottom of the sea and partly from surface waters by both natural and man-made sources (Holm and Persson, 1978). The natural uranium content of freshwater has depended on several factors such as the geological formations in which the groundwater occurs and the size and diversity of aquifer watersheds (Hanson, 1978). Through man's actions, however, uranium has also been introduced to water in an even more concentrated form than would appear as a result of natural weathering. For example, increasing energy demands along with decreasing world supplies of oil and gas have resulted in more abundant sources of energy such as coal being used as an alternative form of energy (MacCormack, 1979). Coal can contain the natural occurring uranium isotopes, ^{238}U and ^{235}U, and associated daughter products (Eisenbud and Petrow, 1964; Van Hook, 1978; Beck et al., 1978; Furr et al., 1979). Averages of approximately 1.0 mg/kg uranium in coal have been suggested (Van Hook, 1978; Anon., 1980). A definite potential exists, therefore, for the further mobilization of both uranium and thorium into aquatic ecosystems through coal combustion, runoff to surface waters and leachate intrusion into groundwater. It is evident from the data presented, however, that more research has been directed towards the chemical form, bioavailability and toxicity of uranium as it is presented in the natural waters than to contaminated industrial wastewaters.

The reported uranium concentrations in various water types and locations are summarized in Table 2. It appears that natural surface waters usually contain low uranium concentrations (0.0001 to 0.0002 mg/L) whereas surface waters in contact with uranium mineralization are usually higher (0.050 to 0.600 mg/L). The average amount of uranium in freshwater may range from 0.0001 to 0.010 mg/L compared to a range of 0.000 36 to 0.0033 mg/L in seawater. Bloch (1980) estimated that the oceans contain over 4 billion tons of dissolved uranium. The average world uranium concentration in water may range from 0.001 to 0.006 mg/L.

Koczy (1963) estimated an average river water value of 0.0005 mg/L in the United States in areas of igneous rocks and clays and suggested higher values may result in waters leaching from carbonate rocks up to a maximum value of 0.200 mg/L. The higher uranium concentrations in United States rivers compared to other world rivers (Table 2) have been explained by the land application of phosphate fertilizers derived from natural phosphate deposits which may have a relatively high natural uranium content and the resulting solublization of soil uranium (Sackett and Cook, 1969; Sackett et al., 1973). Bates et al., (1980) noted that the alkaline lakes of the South Okanagan and Southern Kettle River Valley in British Columbia had higher uranium concentrations (0.010 to 0.030 mg/L), because of the water's increased ionic strength, than the non-alkaline lakes (0.003 mg/L) in the Okanagan Highland region.

Due to the great solubility of natural uranium salts in water, drinking water supplies may accumulate uranium concentrations which are considered to be hazardous to humans (McKee, 1963). Health and Welfare Canada has developed the recommended maximum acceptable level of 0.02 mg/L for uranium (as total uranium) for raw public water supplies and recreational waters. The desirable objective level of 0.001 mg/L or less (as the uranyl ion) has also been established (Anon., 1983).

Following discharge into water, radionuclides may at first remain in solution but may also become associated with mineral sediments, organic debris and aquatic organisms. Uranium has mostly concentrated in sediments with a high organic matter content (Hanson, 1978; Kawabata, 1967). Baturin (1966) reported an enrichment factor of 8 in sediments of the Baltic and Black Seas over the seawater concentration and attributed this to the high hydrogen sulphide concentration in the water. Stream sediments which normally contain from 0.5 to 5.0 mg/L uranium may rise to an average 10 mg/L concentration in uraniferous terrains and to 300 mg/L or more near uraniferous deposits (Bates et al., 1980). Furr et al. (1979) reported that the fly ash pond sediments of a coal-burning electric power generating plant located at a large landfill site in

TABLE 2 URANIUM CONCENTRATIONS IN VARIOUS NATURAL WATERS

Water Type or Location	Uranium Concentration (mg/L)
World Average	0.001
	0.006
Natural Surface Water	0.001
	0.002
Mineralized Water	0.050
	0.460
	0.600
Ocean Water	0.000 36 to 0.059
	0.001 to 0.005
	0.003
	0.003
	0.003
	0.0033
	0.0033
Freshwater	0.0001
	0.0006
	0.001
	0.001 to 0.010
United States River Water	0.0005
Western United States River Water	0.005
India	0.000 01 to 0.007
Black and Mediterranean Seas	0.002
Amazon River	0.000 04

Lansing, New York contained 6.9 mg/L uranium compared to a control pond concentration of 2.1 mg/L.

Hanson (1978) claimed that the concentration of uranium in sediments is indicative of low uranium inventories in biological systems. However, organisms, especially microorganisms, in aquatic environments can absorb and concentrate uranium and its daughters and transform them into more toxic compounds (Pazter, 1976). The

absorption of uranium by aquatic organisms can occur directly from water to the organism or indirectly from one organism to another via food chains (Kovalsky et al., 1966; Fukai, 1966; Baturin et al., 1967; Lopatkina et al., 1970). Resulting pathological effects have been related to both accumulative or additive effects (Patzer, 1976). Aquatic organisms, therefore, can be one of the best indicators of contamination (Havlik, 1971).

The extraction and accumulation of trace elements by aquatic organisms are commonly measured in terms of a concentration factor (CF) which may be defined as the ratio of the concentration of an element in an organism or its tissues to that found in ambient water (Patzer, 1976; Fukai, 1966; Thompson et al., 1977; Polikarpov, 1966). This ratio provides a convenient comparison of the relative accumulation of substances in various organisms (Patzer, 1976; Guthrie, 1970). For example, Chapman et al., (1968) compiled a list of radionuclide concentration factors for edible plants, invertebrates and fish. Concentration factors also enable some form of estimation of uranium concentrations which may eventually arise in biological systems (Pentreath, 1977).

Several sources of variability in radionuclide uptake by aquatic organisms have been suggested: the environmental conditions of the water (temperature, pH and seasonal factors), the physiological conditions of the organisms (species, food habit, age and growth) and the pathway through which the radionuclide reaches the organism (Jinks and Eisenbud, 1972; Bryan et al., 1966; Foster and McCannon, 1962; Nakahara et al., 1977; Nakamura et al., 1977). Kovalsky et al. (1966) claimed that uranium concentration factors in living organisms should show a gradual decrease from one organism to the next up the food chain. In fact, Hanson (1978) reported that the relatively high uranium concentration in water (0.030 mg/L) of Lake Issyk-kul in southeastern Russia decreased regularly along the aquatic food chain of algae → benthic and planktonic animals → fish.

High uranium cumulative capacities have been reported for various species of algae, however, the amount absorbed appears to differ according to species of algae. Sakaguchi et al. (1978) recorded relatively large concentration factors for *Chlorella regularis* (3930), *Chlamydomonas* (2330 to 3400) and *Scenedesmus* (803 to 1290). Morgan (1961) measured a concentration factor of 330 for the algae *Ochromonas* in 48 hours. Justyn (1976) discovered that the green algae *Tetraspora*, collected directly from uranium mine water in Czechoslovakia, accumulated the highest uranium concentration (800 mg/L), whereas, an algae from the genus *Lemanea* contained only 0.20 mg/L uranium in localities unaffected by uranium mining activities. Justyn also found a linear relationship between the uranium content in water and the algae.

The freshwater green algae *Chlorella vulgaris* can also rapidly absorb large amounts of uranium and is not affected by light, temperature or metabolic inhibitors. Uranium uptake by *C. regularis* was inhibited by carbonate ions but increased substantially in decarbonated seawater. The following list represents the uranium cumulative capacity of some algae in decreasing order: *Synechococcus* > *Chlamydomonas* > *Chlorella* > *Dunaliella* > *Platymonas* > *Calothrix* > *Porphyridium* (Sakaguchi et al., 1978).

Hoffman (1942) observed that most of the uranium in the River March between Czechoslovakia and Germany, 0.001 mg/L was absorbed by algae yet toxic effects were not evident. De Jong (1965) showed that the highest uranium concentrations tolerated by *Chlorella vulgaris* ranged from 1.0 to 10 mg/L. Bringmann and Kuhn (1959) observed the first toxic effects of uranyl nitrate on the algae *Scenedesmus* at a concentration of 22 mg/L. O'Kelley (1976) demonstrated that two species of *Chlorococum* were sensitive to powdered uranium oxide at a 0.1 percent concentration. One of the *Chlorococcum* species was also inhibited by a uranyl nitrate molarity of 10^{-4} while the other was inhibited by a molarity of 5×10^{-5}.

Pshenin (1962) concluded that some marine nitrogen-fixing microbes *Torulopsis* and *Rhodotorula* can accumulate significant quantities of uranium from very weak uranium solutions (0.0012 mg/L), equivalent to the natural concentration of uranium in the sea. However, Kharkar et al. (1976) recorded a uranium concentration factor of only 0.17 mg/L for zooplankton, predominantly calanoids and cyclopoids. Gross and Koczy (1946) claimed that uranium levels greater than 1.100 mg/L severely decreased diatom survival. Bringmann and Kuhn (1959) reported that toxic effects of uranyl nitrate on the bacteria *Escherichia coli* first became evident at concentrations of 1.7 to 2.2 mg/L. They also determined that uranyl nitrate concentrations of 28 mg/L and 13 mg/L produced a threshold effect on the protozoan, *Microregma* and freshwater crustacean, *Daphnia magna*, respectively.

Aquatic plants have often acted as indicators of uranium mineralization because they are constantly exposed to, and capable of, accumulating large amounts of uranium through their leaves. Whitehead and Brooks (1971) conducted a preliminary uranium survey of the Lower Buller Gorge Region of New Zealand by comparing uranium concentrations (0.7 to 86 mg/L) in aquatic bryophytes (mosses). Justyn (1976) also found the aquatic bryophytes to have high uranium cumulative capacities by observing the aquatic moss *Fontinalis antipyretica* living directly in uranium ore minewater (800 mg/L uranium). Higher aquatic plants (*Callitriche*, *Batrachium*) survived in localities with even a higher uranium content. Justyn also discovered a linear relationship between the

uranium content in the water and in bryophytes and higher plants. Chapman et al., (1968) reported a uranium concentration factor of 1000 for both marine and freshwater plants.

Sago pondweed (*Potamogeton pectinatus*), dragonfly nymphs (Libellulidae: *Platemis lydia*) and polliwogs (*Rana clamitans*) collected from the fly ash pond of a Lansing, New York coal-burning electric power generating plant contained higher uranium concentrations than those samples from the control pond (Table 3). The red spotted newts (*Notophthalmus viridescens*) from the control pond, however, had a higher content (Furr et al., 1979). Muskrat (*Ondatra zibethicus*) liver concentrations of uranium were identical for both sampling locations.

TABLE 3 URANIUM CONCENTRATIONS OF ORGANISMS IN A FLY ASH POND AND A CONTROL POND AT THE MILLIKEN ELECTRIC POWER GENERATING PLANT, LANSING, NEW YORK (Furr et al., 1979)

	Uranium Concentration (μg/g) dry weight	
Organism	Control Pond	Fly Ash Pond
Sago Pondweed	0.4	1.5
Dragonfly Nymphs	0.1	0.5
Polliwogs	0.9	1.8
Red-Spotted Newts	0.5	0.2
Muskrat (liver)	0.2	0.2

Hamilton (1972) reported a uranium concentration of 0.0002 mg/kg for bulked samples of herring and cod. Risik (1973) presented the most complete set of data for Black Sea fish. Whole body concentrations ranged from 0.000 12 mg/kg for *Uranoscopus scaber* to 0.000 83 mg/kg for *Trachurus mediterraneus*. Lake Whitefish, Northern Pike, Rainbow Smelt and Yellow Perch collected from non-industrialized and heavily industrialized freshwater regions of Canada contained muscle residues of less than 1.0 to 3.0 mg/kg (Uthe and Bligh, 1971). Justyn and Lusk (1976) showed a greater uranium content in fish (1.5 mg/kg) collected from a stream in Czechoslovakia affected by uranium ore mining and milling compared to the natural background content (0.04 to 0.40 mg/kg). Cherry et al. (1976), on the other hand, found relatively low uranium levels present in fish inhabiting

a drainage system that received a high coal ash concentration at one end and thermal discharges at the other.

Uranium residues in fish appear to vary considerably from organ to organ (Pentreath, 1977). Justyn and Lusck (1976) and Kovalsky et al. (1966) reported that major uranium accumulation occurs in the supporting covering tissues rather than in muscular tissues. Poston (1982) also suggested that surface absorption may contribute to the total body burden, however, the majority of uranium and thorium accumulation is located in the gastrointestinal tract and the relatively small amount retained in the carcass is probably in bone. Similarly, Sullivan (1980) claimed that uranium and thorium accumulation in mammals is primarily in bone. Poston (1982) concluded that under their prescribed conditions, neither thorium nor uranium exhibited a great propensity to accumulate in fish tissues.

Few data have been obtained on the effects of body size and temperature on uranium accumulation in fish (Pentreath, 1977). Justyn and Lusck (1976) found a positive correlation between the duration of fish exposition time spent by individuals in a contaminated environment and uranium body content. Pentreath (1977) related the difficulty of estimating uranium concentrations in fish to the time lag which results from food chain accumulation. Kovalsky et al. (1966) on the other hand, claimed that differences in uranium accumulation depended on the individual food chain type (i.e., herbivorous or detritivorous vs. predatory). Poston (1982) concluded that the primary route of uranium uptake in fish is by gut absorption, although the amount retained in tissues is relatively small. Uranium distribution in fish organs and tissues, therefore, corresponds to the amount of uranium absorbed with their food. Chapman et al. (1968) and Thompson et al. (1972) calculated a uranium concentration factor of 10 for marine and freshwater fish.

The toxicity of natural uranium to fish appears to depend primarily on the pH, alkalinity and hardness of the water (Tarzwell and Henderson, 1956). Table 4 presents the reported data on the toxicity of uranium compounds to fish. Uranium appears to be relatively toxic to fish, more so in soft water than in hard water, with a 96-h TLm value (concentration which kills half the fish in 96 hours) of approximately 3.0 mg/L (Tarzwell and Henderson, 1956; Tarzwell, 1956; 1957; 1958).

Till et al. (1976) failed to establish a conclusive upper limit for the chemical toxicity of uranium to developing carp eggs. Hatching and survival of carp eggs were not affected by 60 mg/L uranium and a 76-percent hatch resulted at a 70 mg/L uranium concentration. It appears, therefore, that the carp eggs were relatively insensitive to

TABLE 4 TOXICITY OF URANIUM COMPOUNDS TO FISH (Tarzwell and Henderson, 1956)

Uranium Concentration (mg/L)	Chemical Form	Organism	Exposure Time (h)	Exposure End	Water Type
135.0	Uranyl Sulphate (UO_2SO_4)	Fathead Minnow (*Pimephales promelas*)	96	TLm*	Hard
2.8	Uranyl Sulphate (UO_2SO_4)	Fathead Minnow	96	TLm*	Soft
3.0	Uranyl Nitrate ($UO_2 (NO_3)_2$)	Fathead Minnow	96	TLm*	Soft
3.7	Uranyl Acetate (UO_2AC_2)	Fathead Minnow	96	TLm*	Soft
3.0	-	Fish	-	Toxic	Soft

*Note: exposure ended when half of the fish died

uranium toxicity. The formation of a fertilization membrane in *Urechis* eggs was inhibited, however, at a uranyl nitrate seawater concentration of 250 mg/L, the inhibition seemed to be reversible (Koenuma, 1956).

Thorium. Thorium, the second member of the actinide series of elements, occurs naturally as ^{232}thorium (^{232}Th), however, small amounts of ^{230}thorium (^{230}Th), a daughter product or ^{234}uranium (^{234}U) may be found (Till et al., 1976). Both ^{232}Th and ^{230}Th decay by emitting an alpha particle and have half-lives of 1.41×10^{10} and 8.0×10^{4} years, respectively. ^{232}Th undergoes 6 alpha and 4 beta decay steps before becoming the stable ^{208}lead (^{208}Pb) isotope as shown in Figure 2. Since ^{232}Th is significantly more abundant than ^{230}Th, this discussion will focus on ^{232}Th unless otherwise stated.

Thorium is currently thought to be three times as abundant as uranium. It is commonly found in the aquatic environment as the tetravalent ion which, unlike the uranyl ion, cannot be oxidized to a hexavalent state (Sheppard, 1980). Choppin and Morse (1981) suggested that the affinity of ions for solid surfaces in the aquatic environment generally increases with increasing ionic charge. This is evidenced by the relative

abundance of the divalent uranyl ion in water whereas the tetravalent thorium ion is usually quickly adsorbed or easily precipitated as a hydrolysate because of its very high ionic potential (Adams et al., 1959; Pentreath, 1977). Therefore, thorium is usually found in low concentrations in water (Garner, 1972) and a low thorium/uranium ratio in water solutions is often observed (Adams et al., 1959). Moore and Sutherland (1981) reported thorium water levels in Great Bear Lake near an abandoned uranium mine to be generally below detectable limits, reflecting the strong chemical bonding characteristics of the sediment.

Thorium has a very low abundance in freshwater (1.0×10^{-5} to 1.0×10^{-4} mg/L) and an even lower abundance in seawater (1.0×10^{-6} mg/L) (Bates et al., 1980). Goldberg and Koide (1962) found small quantities of dissolved or suspended thorium in ocean water (5.0×10^{-5} mg/L). Adams et al. (1959) reported a range of thorium concentrations in seawater of 4.0×10^{-8} to less than 5.0×10^{-4} mg/L. Hansen and Stout (1969) stated that ^{230}Th produced by ^{234}U decay usually settles to the bottom because of the affinity of thorium for solid-phase material. Mackenzie et al., (1979) reported a radioactive disequilibrium in seawater occurs as a result of thorium's very low solubility such that ^{228}radium (^{228}Ra) and ^{224}radium (^{224}Ra) in seawater are virtually unsupported by their thorium parents.

Data concerning thorium levels in sediments appear to be very limited. Bates et al. (1980) believed that the heavy mineral fractions of stream sediment retain thorium as well as certain clay or alumina-rich fine fractions. Moore and Sutherland (1981) reported significant negative correlations between ^{232}Th and ^{228}Th concentrations, the distance from an abandoned uranium mine in Great Bear Lake, and the organic content of the sediment. Precipitates of thorium from warm and hot springs have reportedly ranged from 150 mg/L to 12 300 mg/L (Bates et al., 1980). Sediment, collected from the fly ash pond of the Milliken Station coal-burning electric power generating plant in Lansing, New York had a thorium concentration of 48 mg/kg whereas the sediment from the control pond contained 11 mg/kg (Furr et al., 1979).

Like uranium, thorium does not appear to be an essential material for any aquatic organism or organic process (Bates et al., 1980). Bringmann and Kuhn (1959) reported a thorium concentration of 0.80 mg/L began to show toxic effects on the bacteria *Escherichia coli* after 96 hours at 27°C. They also observed the first toxic effects on the green algae *Scenedesmus* at thorium concentrations of 0.40 to 0.80 mg/L after 96 hours at 24°C. A thorium nitrate concentration of 25 mg/L was deleterious to the protozoa *Microregma*, whereas 1000 mg/L of thorium nitrate was not acutely toxic to

the small crustacean *Daphnia magna* at 23°C for 48 hours. De Jong (1965) found the freshwater algae *Chlorella vulgaris* could tolerate maximum thorium concentrations of 0.01 to 1.0 mg/L over a 3 to 4 month period. Kharkar et al., (1976) stated that the ^{228}thorium concentration factor for zooplankton relative to seawater was 20. Algae (*Zygnema*), dragonfly nymphs (Libellulidae: *Platemis lydia*), sago pondweed (*Potamogeton pectinatus*) and polliwogs (*Rana clamitans*) had considerably higher thorium concentrations when collected from the fly ash pond of the Milliken Station coal-burning electric power generating plant than those sampled from the control pond (Furr et al., 1979) (Table 5). Red-spotted newts and a muskrat collected from the control pond, however, had unexplainable higher thorium concentrations than those sampled in the fly ash pond.

TABLE 5 THORIUM CONCENTRATIONS OF ORGANISMS IN A FLY ASH AND A CONTROL POND AT THE MILLIKEN ELECTRIC POWER GENERATING PLANT, LANSING, NEW YORK (Furr et al., 1979)

	Thorium Concentrations (µg/g) dry weight	
Organism	Control Pond	Fly Ash Pond
Algae	1.80	8.80
Dragonfly Nymphs	0.40	0.80
Sago Pondweed	0.40	7.60
Polliwogs	3.30	9.20
Red-spotted Newts	1.70	1.20
Muskrat (Liver)	0.40	0.20

In a river system that received a high coal ash concentration at one end and thermal discharges at the other, Cherry et al. (1976) found the only fish species present was a preditor, the mosquitofish (*Gambusia affinis*) which contained relatively low levels of thorium. Doudoroff and Katz (1953) reported that 18 mg/L of thorium chloride was the lethal concentration for three mature small freshwater fish (*Orizias*) exposed for 24 hours to only 20 mL of test solution.

Summary. At the present time there are seemingly conflicting reports on the chemical toxicity of uranium and thorium. There is a paucity of data at present to accurately assess the environmental effects of the chemical toxicity of naturally

occurring thorium and uranium on aquatic ecosystems. The information available, however, indicates that released uranium and thorium will ultimately reside in sediments, organic debris or aquatic organisms. Sediments have been neglected, on the whole, as a depot of both uranium and thorium in aquatic ecosystems. As indicated in the literature, a variety of freshwater and marine organisms have accumulated uranium and thorium and several toxic concentrations have been suggested. The chemical toxicity of uranium is thought to be the principal concern rather than its radioactive properties. Although thorium is more abundant naturally than uranium, it appears to be less bioavailable in the water column due to its stronger chemical bonding properties. Local environmental conditions and physiological factors appear to have strongly influenced accumulation of uranium and thorium. In general, the limited data and different test procedures used to date make the comparison of tests and results difficult and evaluations only tentative.

The contribution of radioactive emissions from these substances to the observed toxic effects over long periods has not yet been ascertained but it is thought that they are minimal. In fact existing guidelines are based on chemical rather than radiotoxicity. However, unlike human toxicity criteria which are based on ingestion or inhalation, aquatic organisms not only ingest and inhale but are surrounded by the same levels continuously in their environment resulting in internal and external exposure. This is significant when the physiological differences between aquatic species and humans are considered. Although the penetration of radioactive emissions remains essentially constant, greater exposure to critical internal organs is possible, due to the smaller body size of aquatic organisms.

2.2 Bioaccumulation of Radionuclides

When chemical elements or compounds are released into the environment, they quite often become dispersed and diluted, but they may also become available for uptake by living organisms. Uptake of an element by an organism that results in an internal concentration greater than the element's concentration in the environment is called bioaccumulation; therefore, different levels of concentration are observed in different species.

The ratio of the concentration of an element in an organism to that in the abiotic environment is called the "concentration factor" or "bioaccumulation factor". For example, the concentration factor of a substance in lake trout would be determined by:

$$CF_t = (R_t)/R_w)$$

where: CF_t = concentration factor for substance R in the lake trout

(R_f) = substance concentration (in terms of fresh weight) in the lake trout

(R_w) = substance concentration in water

Concentration factors can be determined for whole organisms or for individual tissues within organisms, such as bone, muscle or liver. The use of concentration factors to describe bioaccumulation depends on the assumption that the bioaccumulation is occurring in a steady state environment, that is, uptake by individual species/tissues does not vary over time. Figure 5 is a schematic illustration of bioaccumulation by aquatic organisms under steady state conditions (Lusk and Swanson, 1981).

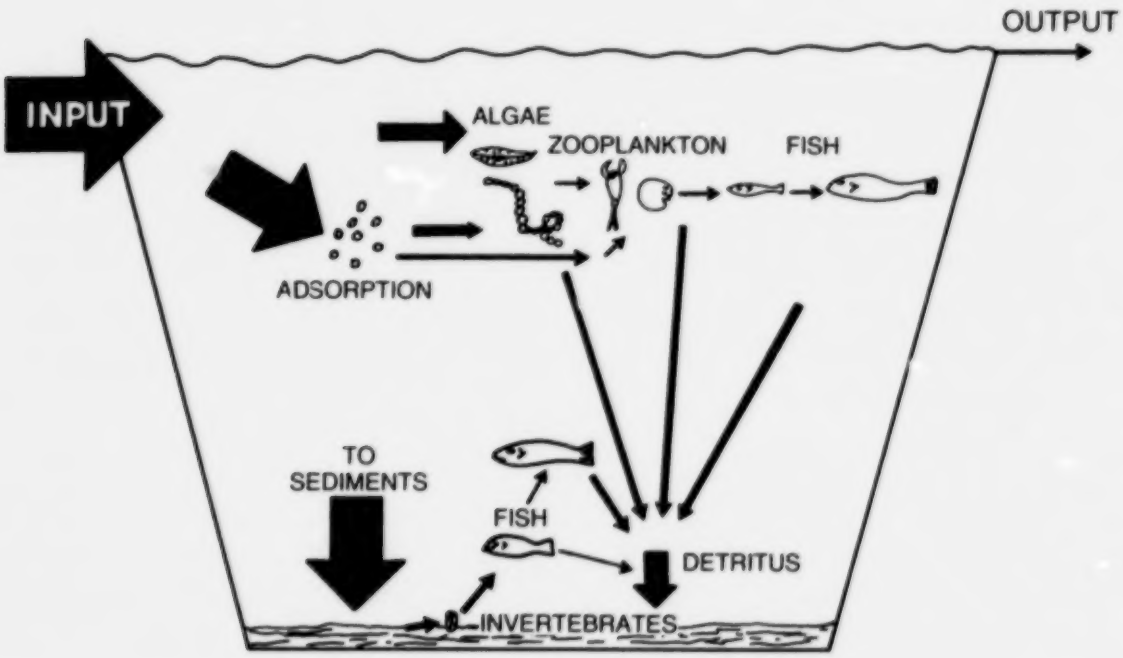


FIGURE 5 STEADY - STATE DISTRIBUTION OF RADIONUCLIDES IN AN AQUATIC SYSTEM (Lush and Swanson, 1981) The relative width of the arrows and importance of sediments as a source of contaminants.

The bioaccumulation of substances within food chains may or may not lead to "biomagnification", which is increasing concentration of the element with each step from organism to organism or from prey to predator up the food chain. The element cesium, for example, increases in concentration (bioaccumulates) from the concentration found in the water. Ninefold increases of cesium have been reported through the plant-deer-cougar chain, and fourfold increases have been reported in the lichen-caribou-wolf chain, along with an increase by a factor of three of the concentration in humans compared with that in their food (Garner, 1972). The cesium radionuclides, however, are associated with man-induced fission activities and do not occur in the natural uranium and thorium decay chains examined here. Although the naturally-occurring radionuclides (those in the uranium and thorium decay chains) have not been studied as extensively as the fission products, available evidence shows a decrease in concentration with increasing trophic level. For example, a two- to four-fold decrease in concentration factors has been reported for ^{210}lead and ^{210}polonium in the lichen-caribou-man chain (Holtzman, 1968), and a ten-fold decrease has been reported for ^{226}radium, ^{210}lead, and uranium in the insect-forage fish-large fish food chain (Swanson, 1981). This suggests that natural radionuclides are bioaccumulated but not biomagnified through the food chain.

Irrespective of whether substance concentrations continue to increase in higher tropic levels in terrestrial food chains, bioaccumulation by organisms at the first trophic level leads to mobilization of substances within ecosystems. Thus the substances become available to consumers, leading to levels in organisms that are significantly above "background" levels in the abiotic environment. In aquatic systems this may also lead to increased levels of external exposure:

1) through substance uptake, organisms create a cycling of these elements from the environmental media (air, soil, water) through food chains and back to the media;
2) in so doing, organisms may prevent the "locking" of substances into "environmental sinks" such as lake bottom sediments;
3) substance levels within organisms in the food chain may adversely affect individual or population "fitness" in the long-term; and
4) food chain transfer may also eventually lead to man.

2.2.1 Mechanism of Bioaccumulation. Bioaccumulation is a natural process; the ability to concentrate and regulate the cycling of certain elements is essential to the survival of all life on earth. Most species have evolved the ability to selectively extract the various elements required for life and vary the bioaccumulation factor in response to

environmental availability and physiological need. At the other extreme, systems have been evolved to selectively excrete various trace elements when the body loadings become higher than necessary. The net result is what may be termed a normal metabolic functioning range, which is related to the environmental availability of most trace elements. For some elements such as sodium, which is an essential element for life (macronutrient) and is both available and required in fairly large quantities, the band may be relatively wide, whereas for other elements such as selenium, which is required only in small quantities (micronutrient) the normal band may be relatively narrow (Figure 6). There are also a number of elements which no known life functions require and which are not essential for life.

There is no evidence that radioactive elements such as uranium, thorium, radium, or others are essential trace elements. The uptake of many radionuclides may be related to their chemical similarity to elements that are essential nutrients. For example, ^{226}radium and calcium are chemical analogues; organisms do not distinguish between the two in terms of uptake. Therefore, if both calcium and ^{226}radium are present in ingested food, both will be absorbed from the gut according to the physiological needs of the organism for calcium and incorporated into tissue (in this case, into bone) (Eisenbud, 1973).

The uptake of some other radionuclides does not appear to be related to similarity with essential nutrients. For example, uranium has no reported chemical analogue. The bioaccumulation of this group of radionuclides may be due to passive uptake from air, soil, water or food. Accumulation may also be related to other needs of the organism, such as water. In plants, uranium uptake may be related to water stress; desert plants have higher uranium concentrations than humid-area plants (Sheppard, 1980). The bioaccumulation factors for radionuclides with no recorded chemical analogues or "carriers" are generally much lower than those for radionuclides that do have analogues. For example, ^{226}radium bioaccumulation factors were 10 to 50 times higher than uranium factors in lake whitefish and white suckers from northern Saskatchewan (Swanson, 1982).

2.2.2 Factors Affecting Bioaccumulation. The uptake of radionuclides by terrestrial and aquatic organisms appears to be influenced by numerous factors including:

1) Concentration and Behaviour of the Radionuclide in the Environment

It would appear that the uptake of naturally occurring radionuclides by organisms is not necessarily linearly related to the environmental concentration. Generally uptake appears to decrease with higher environmental concentration (Patzer, 1976).

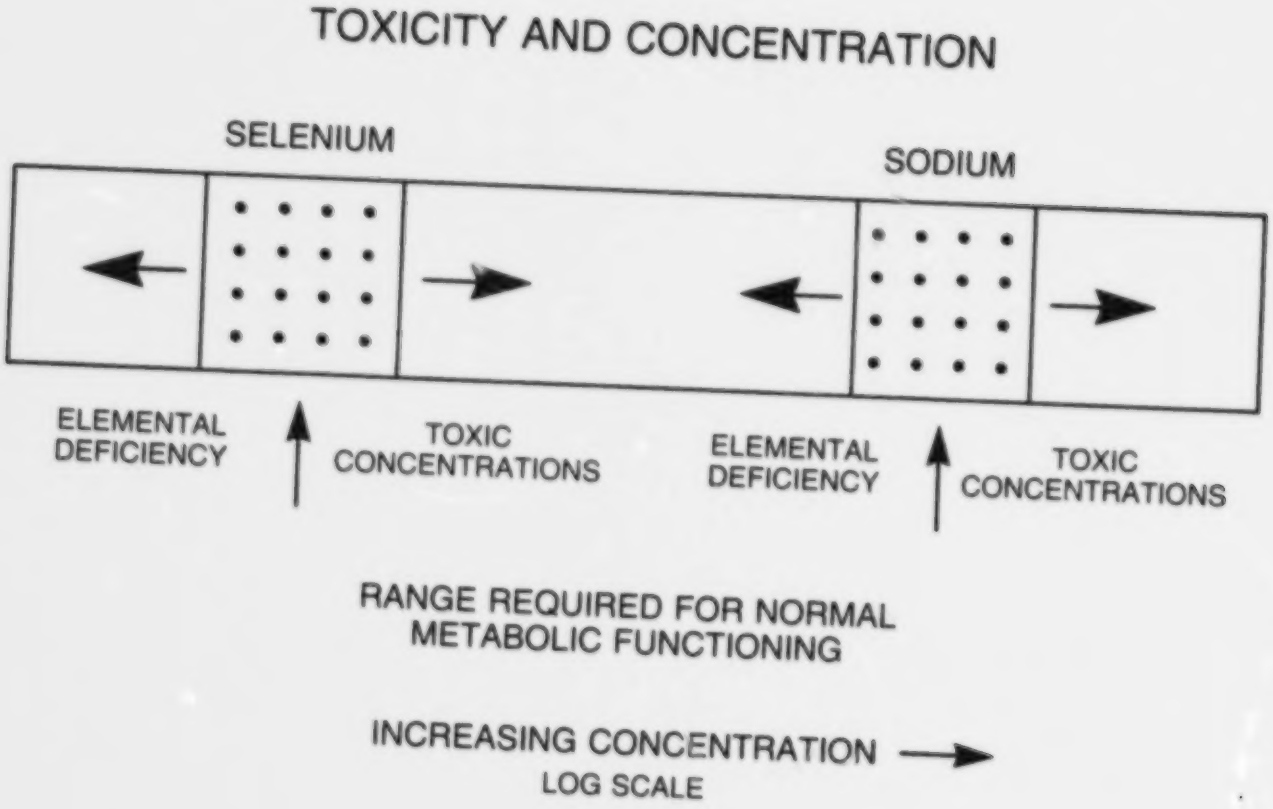


FIGURE 6 NORMAL METABOLIC FUNCTIONING FOR A MACRONUTRIENT (Sodium) AND A MICRONUTRIENT (Selenium) (Lush and Swanson, 1981)

In addition, natural radionuclide levels in the environment vary according to their position in the decay chain and their half-lives, therefore, levels of one radionuclide may not be in equal proportion to that of another in the same decay series. For example, ^{210}lead and ^{210}polonium are commonly present in greater amounts in the environment than their parent radionuclide, ^{226}radium. This occurs because ^{226}radium first decays to ^{222}radon, a noble gas which is easily translocated from its parent and dispersed over a wide area. The radon eventually decays through a series of short-lived daughters to ^{210}Pb, which is then taken up in amounts that can be quite unrelated to local ^{226}radium levels. ^{210}Polonium is the daughter of ^{210}lead, but its behaviour in food chains like lead in comparison to radium is not necessarily correlated with its lead precursor because of their different chemistries and metabolic properties (Holtzman, 1969).

2) Environmental Concentration

In general, the greater the concentration of the stable isotope or chemical analogue the lower the accumulation of the radioactive isotope analogue. For example, it has been shown that a change in calcium concentration from 1 to 10 mg/L will reduce the concentration factor for strontium, a calcium analogue, by approximately five (Ophel, 1979). It is assumed that a similar reduction would occur for radium uptake. In soils, it has been shown that a high soil calcium concentration results in lower radium migration and uptake by plants (Sheppard, 1980).

3) Chemical Form of the Radionuclide in the Environment

Radionuclides can exist in several forms (or species) including: dissolved ionic species, complexes with organic molecules, adsorbed to solids, precipitates and coprecipitates, incorporated in solid biological materials, and incorporated in crystalline structures (Vanderploeg et al., 1975). Each of these forms have different availability to organisms and may also have different chemical toxicities. For example, radium adsorbed as exchangeable ions on the surface of soil particles is much more available to plants than radium which is strongly bound to organic humic material (Sheppard, 1980). It should be noted, however, that regardless of the chemical form of the radionuclide, its radioactivity and its potential for radiation damage to organisms remains the same.

4) Characteristics of the Environmental Medium in which Radionuclides are Found

In aquatic systems, radionuclide uptake varies with turbidity, pH, total dissolved solids, light and temperature (Vanderploeg et al., 1975; Lush and Swanson, 1981). For example, uptake is greater in clear, soft water than in turbid, hard water and uptake is greater in warm water than in cold (Eisenbud, 1973). In terrestrial systems, soil type, soil moisture and soil chemistry affect availability and uptake of radionuclides. For example, plants absorb more uranium from calcium-uranium carbonate and limestone type soils than from sandstone and shale (Sheppard, 1980).

5) Spatial and Trophic Niche of the Organism Accumulating Radionuclides

In both terrestrial and aquatic systems, radionuclide accumulation appears to vary with organism species. This variation is often related to the "spatial niche" (the habitat) of the organism. For example, bottom-feeding fish such as suckers accumulate higher levels than predatory fish such as lake trout; the higher sucker levels are thought to be due to the contact with sediment which often contains concentrations of radionuclides many times that of the overlying water (Swanson, 1981). Radionuclide levels can also be related to mode of uptake. Because of their large surface area and because they obtain all nutrients from the air, lichens have exceptional ability to accumulate air-borne pollutants such as plutonium (fission product) or ^{210}lead. Similarly, algae and mosses, which absorb nutrients directly from the surrounding medium, accumulate greater amounts of radionuclides than higher plants. The "trophic niche" or level in the food chain, also influences the level of bioaccumulation. For some radionuclides, such as ^{137}cesium, (fission product) organisms at higher trophic levels have higher concentrations while, for other radionuclides such as uranium or ^{226}radium, there is a progressive decline with increase in trophic level. The behaviour of individual radionuclides in food chains is related to such factors as the degree of homeostatic control exerted by the organism over the radionuclide (and its carrier element or analogue), the presence of "metabolic sinks" (such as undigestible skeletal material) midway in the food chain, and the metabolic turnover rate (assimilation vs elimination) at the various trophic levels.

6) Physiological Differences Between Species, Between Individuals of the Same Species and Within Tissues of the Same Individual

Differences in bioaccumulation between species which occupy similar spatial and trophic niches may be due to differences in physiology. For example, one species of grass growing on uranium tailings, red fescue, takes up much more radium than red canary grass growing on the same tailings (Moffat and Tellier, 1977). Radionuclide uptake of individuals within a species can also vary considerably, due to physiological differences with age, sex or size (Patzer, 1976). Uptake by different tissues within organisms can vary according to tissue function, relative metabolic activity, or the similarity between a radionuclide and an element essential to the structure or function of a particular tissue. For example, uranium levels in trees have been found to be highest in growing tips of twigs, followed by bark, leaves and wood (Sheppard, 1980; Dunn, 1981). ^{226}Radium and its daughter ^{210}lead concentrate in animal bone since radium is analogous to calcium. Presumably the radium, taken up as a calcium analogue, later decays to lead.

2.2.3 Effects of Radionuclides Within Organisms. Radionuclides taken up via bioaccumulation from the environment and retained in an organism will deliver chronic, low-level radiation continuously over a whole life cycle. It is now generally accepted that all radiation, no matter how small the amount, may have an effect on organisms (Anon., 1977). The detection of these effects in individuals and populations, however, is extremely difficult, due to the multitude of environmental factors influencing organisms and populations and the potentially different types of damage from decay event to decay event. The nature of the effect is also variable since it depends on the type of damage caused by the radiation event. This, in turn, is governed by the sensitivity of the affected biological material which has been irradiated.

The effects of radiation may be expressed at the organism, population or ecosystem levels. The tissues most likely to show the earliest effects of radiation are those with rapidly dividing cells such as gonadal tissue or bone marrow. Effects of radiation are shown early in the young, due to rapid growth rates. The effects of chronic low-level radiation at the organism level are usually looked for as increased mutations and/or increased malignant cancers particularly in the young. At the population level, higher mutation rates may eventually lead to a compensatory increase in production of young, causing greater stress on adult individuals and higher overall mortality. In addition, the "fitness" of the population in terms of its adaptation to the environment or

ability to continue surviving may be reduced because of physiological, morphological or behavioural changes induced by radiation damage. Changes in the "gene pool" of populations is thought to be the primary long-term hazard of chronic radiation (Ophel, 1979). Ecosystem structure or species population can be altered due to effects of radiation. Should a system receive a higher level of radiation than that under which it evolved, adaptations and adjustments will occur that may include elimination of the most exposed or sensitive strains of species, alterations of predator-prey equilibria and changes in productivity (Odum, 1971).

2.2.4 Factors Affecting Radiotoxicity of Radionuclides. The radionuclides generally considered to be of most concern currently when considering bioaccumulation or damage from within, are those emitting high-energy alpha radiation. Alpha radiation consists of alpha particles (2 protons and 2 neutrons). These particles are relatively slow moving and have a very short range, but they leave a dense trail of ionization and their local effect on living tissue in their path may be greater than that of other smaller particles of longer path length. The naturally occurring radionuclides emitting high-energy alpha radiation include ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{222}Rn, and ^{210}Po in the uranium decay chain and ^{232}Th, ^{228}Th and ^{224}Ra in the thorium decay chain. Of these, the nuclides with extremely long half-lives, such as ^{238}U (4.5×10^9 years), ^{234}U (2.5×10^5 years) and ^{232}Th (1.4×10^{10} years) are presently considered to be of less radiotoxicity concern because of their low specific activity. Specific activity is an expression of the amount of radiation produced per gram of element. In the slow-decaying long-lived radionuclides, the amount of radiation being emitted is much smaller per unit of time per gram than in radionuclides with shorter half-lives.

In addition to the type of radiation emitted, the behaviour of the radionuclide within the organism is important. Some radionuclides are analogous to essential nutrients. For example, ^{226}Ra, is analogous to calcium and is incorporated into bone where the radiation can affect bone marrow cells and bone-lining cells (Eisenbud, 1973). Others are incorporated into internal organs; for example, ^{210}polonium is concentrated in the spleen and kidney of humans (Eisenbud, 1973).

The length of time required for the organism to eliminate or excrete radionuclides is also a factor determining overall effect on the organism. This time period is called the "biological half-life", that is, the time required to eliminate one-half of the radionuclide burden. The radionuclides with long biological half-lives relative to the organism's life can cause greater damage. ^{226}Radium and ^{210}lead, have biological

half-lives of 10 to 12 years; these nuclides can therefore cause more overall damage than ^{238}uranium, with a whole body half-life of 100 days (Eisenbud, 1973).

2.2.5 Examples of Radiotoxicity. Radiation emitted from radionuclides causes damage because it causes ionization. For example, electrons are removed from a target atom or molecule to form a positively charged ion. Ionization within body tissues causes a change in the structure of important molecules such as deoxyribonucleic acid (DNA) (UNSCEAR, 1977). Molecules of DNA carry the genetic information necessary for appropriate cell development, maintenance and division. Radiation can destroy or alter some of the information in these molecules, resulting in cell death or a change in form leading to cancer or genetic effects in subsequent generations (Bayda, 1978).

The effects of radiation damage can be divided into two categories: somatic and genetic (Rothschild, 1973). The effects which become apparent in the exposed individual are somatic, while genetic effects are observed in the offspring.

This discussion is limited to the so-called chronic or late somatic and genetic effects of long-term, low-dose radiation. To date the most important late somatic effect of low doses of radiation appears to be the induction of malignant disease, as shown by the increased incidence in exposed human populations (UNSCEAR, 1977). The most commonly observed somatic effects in non-human populations have been those on developing embryos. For example, aquatic organisms in White Oak Lake, Tennessee, received doses from fission and/or activation products approximately 1000 times background for the area for several years. Studies revealed an increased number of dead embryos and abnormalities in mosquitofish (*Gambusia affinis*) populations (Blaylock and Trabalka, 1978). The White Oak Lake fish produced more eggs per female (increased fecundity), presumably in response to greater embryo mortality. Ten years after the first series of studies on the lake, dose rates had decreased by an order of magnitude. The fecundity of the mosquitofish had returned to control levels; however, the frequency of dead embryos and abnormalities was still significantly elevated. Studies of the effect of chronic low-level gamma radiation on chinook salmon (*Oncorhynchus tshawytscha*) in the Columbia River revealed increased abnormalities in young fish at all dose rates, however, the number of adults returning to spawn was not affected (Donaldson and Bonham, 1970). Several Russian studies found increased mortality, smaller overall size of young, and increased malformations in ocean fish species exposed to radiation levels only slightly above background (Anon., 1976). Some subsequent studies, however, have not produced similar results yet (Blaylock and Trabalka, 1978).

Developing mammalian embryos appear to be very sensitive to radiation. Radiation in the early states of embryogenesis may cause death of the embryo, or failure of implantation. Irradiation after implantation and during the period in which body structure is becoming differentiated and organs are developing causes a wide range of malformations in a number of mammalian species. These effects have been proven at doses above 300 times background level. However, low-dose radiation may also impair normal fetal growth and this impairment may persist after birth (UNSCEAR, 1977).

The genetic effects of low-dose radiation are related to DNA molecules, or to the induction of chromosome aberrations (changes in the structure or number of chromosomes). When such changes occur, they may be passed on to offspring in which the mutant characteristic may ultimately be expressed as they grow. Chironomid (midge) larvae have frequently been the focus of studies of genetic damage caused by radiation due to the large size of their salivary gland chromosomes. Chironomids exposed to radiation doses of 1000 times over background exhibited a high frequency of chromosomal aberrations (Nelson and Blaylock, 1963). In a similar study, Blaylock (1966) found an increased frequency of chromosome aberrations in chironomids in White Oak Lake. These genetic aberrations did not become established in the population, it appears that they were rapidly eliminated by natural selection or genetic drift in subsequent generations.

A number of indirect genetic effects may also be observed as a result of ionizing radiation. Deviations from the original systematic description of an organism can occur. For example, mutations affecting the colour-pattern of guppies (*Lebistes reticulatus*) in offspring of males exposed to gamma rays have been recorded (Purdom and Woodhead, 1973).

Radiation effects on genetic material may eventually influence the viability of a species (Ophel, 1979). In an environment in which organisms are experiencing greater than natural exposure to radiation, fitness may be altered. This is because the inherited genetic constitution, before the increased irradiation, would presumably have been close to the optimum required for survival in the particular environment (Barclay, 1981). Mutations resulting from enhanced radiation may cause the organism to be less efficient in exploiting the resources of the environment or long-term genetic effects resulting from an increase in deleterious recessive mutations may only become apparent as they gradually increase over many generations and are expressed in homozygotes as malformations of "genetic diseases". This may further reduce the survival potential of a species population (Templeton, 1976).

In summary, the most serious concern demonstrated to date regarding the effects of long-term low-dose radiation on populations appears to be with respect to genetic change. Serious somatic effects which are attributable solely to radioactivity remain to be convincingly demonstrated at doses below 100 to 300 times background. This current deficiency may stem from difficulty in separating chemotoxic from radiotoxic effects and the lack of controlled, long-term studies to date.

The radionuclides of concern with respect to coal-fired power plants are the primordial nuclides, those in the natural uranium and thorium decay chains. This discussion, therefore, deals with studies of such primordial nuclides as distinct from those which are primarily associated with chains from man-induced activities such as nuclear power generation.

2.2.6 Aquatic Systems. Studies conducted in relatively uncontaminated aquatic environments show that natural uranium and thorium series radionuclides are wide-spread in both the environment and biota and contribute a substantial fraction of the present radiation dose level to biota. Bioaccumulation relative to environmental levels (concentration factors) is greatest at lower trophic levels. For example, insect larvae, crustaceans and mussels taken from the Gulf of Finnland had CF's of 1100 to 200 000 while fish (herring, whitefish, pike, salmon, cod) had CF's of 5 to 1000 (Kauranen and Miettinen, 1970). Analysis of samples from the Great Lakes also indicated bioaccumulation but a CF decrease with trophic level. Zooplankton uranium and thorium levels were an order of magnitude above levels in forage fish (spottail shiners, alewife, trout-perch) (Lucas et al., 1970).

Measurements of radionuclide uptake in contaminated environments, for example, near uranium mines and mills, show greater absolute levels than those in unaffected areas, but similar concentration factors and food chain behaviour. A study of ^{226}radium levels in algae, insects and fish downstream of a uranium mill in the Animas River, Colorado, showed levels two orders of magnitude greater than those upstream of the mill (Anderson et al., 1963). Levels were greatest in algae, followed by insects, then fish. Concentration factors, however, were similar in organisms upstream and downstream of the mill. Insects, forage fish and large fish from Beaverlodge Lake, Saskatchewan, a lake receiving discharge from a uranium tailings treatment area, had radionuclide levels one to two orders of magnitude above those in uncontaminated lakes (Swanson, 1982). Levels were greatest in insects, followed by forage fish, then large fish. Concentration factors were similar in organisms from Beaverlodge Lake and control lakes

and were also similar to those found for Animas River biota. The Beaverlodge Lake studies also demonstrated the influence of habitat and food habits on radionuclide uptake; levels in piscivorous lake trout, which fed mainly on plankton-feeding ciscoes, were much lower than levels in bottom-feeding fish such as whitefish and suckers. Low levels in lake trout have also been recorded from contaminated areas of Great Bear Lake, North West Territories (Moore and Sutherland, 1981).

2.2.7 Terrestrial Systems. The most intensively studied aspect of bioaccumulation in terrestrial systems has been the levels found in components of the human diet. For example, studies of the relative contributions to the total uranium intake of inhabitants of a number or U.S. cities showed that potatoes were the major single source, with additional significant contributions made by bakery products, meat and fresh fruit. Drinking water rarely contributes a significant portion of total radionuclide intake, except where local wells and springs have unusually high levels (Garner, 1972). When examining the impact of radionuclide contamination over and above background levels, the first step is often to study levels in foodstuffs known to be significant bioaccumulators.

One of the best known examples of bioaccumulation in foodchains leading to man is the lichen-reindeer/caribou-man pathway. This pathway has been studied for accumulation of natural radionuclides and fission products (such as ^{90}strontium, ^{239}plutonium, and ^{240}plutonium). The pathway is important because of the ability of lichens to concentrate radionuclides in atmospheric fallout. Lichens have a large effective surface area and obtain all their nutrients from the atmosphere. The lichens are an important component of reindeer and caribou diets, which are, in turn, consumed by northern peoples such as Canadian Inuit and Finnish Lapps. Based on measurements of radionuclides in lichens, caribou and human placentas, it was concluded that Inuit could acquire sufficient ^{210}lead to double the total skeletal radiation dose over that of mid-westerners (Holtzman, 1968). Similarly, a reindeer or caribou meat diet for man increases ^{210}polonium body burdens by about two orders of magnitude even though the overall behaviour of most radionuclides (^{210}polonium, ^{210}lead, ^{226}radium and plutonium) in this pathway shows a progressive decline with increasing trophic level (Hill, 1965). Based on the evidence to date, natural radionuclide behaviour in terrestrial food chains would appear to parallel that found in aquatic systems.

2.2.8 Bioaccumulation Near Coal-fired Power Plants. Measurements in environmental samples around coal-fired power plants show the presence of enhanced concentrations of natural radionuclides (UNSCEAR, 1977). Analyses of ^{226}radium, ^{214}lead, and

^{214}bismuth, in fly ash from 18 U.S. coal-fired power plants showed fly ash levels from western plants to be 4 to 12 times higher than in "typical" soils, while levels from eastern plants were 3 to 14 times higher than in soils (Morris and Bobrowski, 1979). Estimates of average uranium and thorium concentrations in fly ash from three standard coal types yielded figures 6 to 17 times typical soil concentrations (Dvorak and Lewis, 1978). Analysis of fly ash from an Ontario coal-fired power plant produced levels of the uranium and thorium series (mostly by natural alpha emitters) 1.5 to 4 times typical soil levels (Greening, 1981).

It is apparent that the release of radionuclides from coal-fired power plants creates a potential for bioaccumulation in terrestrial and aquatic food chains. The magnitude of the problem is related to the behaviour of radionuclides in the coal-fired power plants, the amounts and kinds captured by pollution control equipment before release, the form in which they are released and their mobility once released into the environment.

The relative amounts of radionuclides released as gases, fly ash and bottom ash vary with the chemical and physical properties of the individual radionuclides. For example, ^{210}Pb which is released primarily via fly ash volatilizes readily in the combustion zone, then may begin to condense again on the finer fly ash particles further up the stack (Coles et al., 1978). Radium and thorium appear to be at essentially the same concentration in bottom and fly ash while the behaviour of uranium seems to be intermediate between that of lead and that of radium and thorium (UNSCEAR, 1977). Radionuclides in fly ash which escapes can affect terrestrial and aquatic systems downwind of the plant. The bottom ash, and captured fly ash will primarily affect aquatic systems via surface runoff from ash piles and leaching into groundwater from the disposal area.

The actual radionuclides released from ash piles will vary with radionuclide mobility in the environment and the disposal area. Normally, one would expect the daughters in a radioactive decay chain to be in secular equilibrium with each other. If "x" activity of a parent radionuclide such as ^{238}uranium, is present, then there must also be "y" amount of uranium daughters, such as ^{226}radium or ^{210}lead; there is a constant ratio between the two radionuclides. Radionuclides in environmental samples, however, are seldom in equilibrium because of the variable mobility of individual nuclides. For example, all uranium isotopes are leached from rock and soil faster than the daughter isotopes ^{230}Th, ^{226}Ra, ^{210}Pb and ^{206}Pb. This is because uranium readily forms soluble complexes with sustances commonly found in soils such as carbonate (CO_3^-), hydroxide

(OH^-) or phosphate (PO_4^-) (Sheppard, 1980; Dyck, 1974). ^{226}Radium is relatively immobile in soils except under conditions of low pH and/or high water content (Sheppard, 1980). ^{210}Lead is often quite immobile in parent materials because lead tends to form rather insoluble sulphides and sulphates (Dyck, 1974). ^{210}Pb, however, is often found at higher levels in environmental samples than can be accounted for by the amount of parent isotopes present. This is because ^{210}Pb is a daughter of the gaseous isotope, ^{222}radon. Radon readily diffuses out of its parent material and it and its daughters are dispersed over relatively wide areas. Thus, excess ^{210}Pb is often found in lake or river sediments because of atmospheric deposition via the decay of radon. The variable mobilities of the radionuclides must, therefore, be considered when assessing the impacts of ash piles.

Despite concerns and controversy regarding levels of radionuclides in coal-fired power plant effluents, there have been very few studies involving actual measurement of levels in the environment surrounding power plants. Evaluation of the impact from atmospheric release varies. Estimates of collective doses to humans in the vicinity of power plants have suggested that the additional dose resulting from inhalation and ingestion of activity released into the atmosphere would be very small (UNSCEAR, 1977; Bayliss and Whaite, 1966). It has also been suggested that where actual measurements have been taken in soil, water and vegetation, virtually no enhancement of radionuclide levels above background were found (Wangen and Williams, 1978; Tracy and Prantl, 1981). Wangen and Williams (1978), however, point out that the techniques used may not have been sensitive enough to detect an impact on local soils, and Tracy and Prantl (1981) did not specify the soil or vegetation types analyzed. A model of the suspension and dispersion of ash from uncovered ash disposal piles indicated that annual doses from ingestion of foods grown in the immediate vicinity of ash ponds could reach the same order of magnitude as the maximum permissible level estimates proposed for uranium fuel cycle facilities (Styron et al., 1981). Consequently, there is still a need for systematic studies of specific food chains before the potential for bioaccumulation and enhanced doses to humans resulting from atmospheric releases can be properly assessed.

The impact of fly and bottom ash disposal sites on the environment is also open to question. The release of radionuclides via surface run-off or leaching to groundwater may result in contamination of aquatic habitats and bioaccumulation in aquatic food chains. In addition radon escape from the piles may disperse radon and its daughters over a wide area.

Studies of radionuclide and trace element releases from coal ash piles have illustrated the influence of original coal type, proximity of acquifers and type of soil,

climite, and local water quality. For example, storage of ash from high sulphur, acidic coals in a humid area near a sand aquifer are indicated to result in acidic leachate carrying large amounts of trace elements whereas the storage of ash from low sulphur coals in a dry area over clay soils are indicated to result in a very low volume, less acidic leachate with low levels of trace elements (Davis and Boegly, 1981). A study of leachate from coal ash ponds in Tennessee showed that these coal ash leachates are highly variable, chemically reduced, can be acidic even when generated by alkaline ash, and are likely to be more acidic with higher trace element levels when measured in interstitial water rather than in well samples (Milligan and Ruane, 1980). The study also showed that the mass of trace elements in the ash pond leachate entering adjacent surface water was negligible when compared to the mass discharged by the once-through ash pond surface overflow even though concentrations in the groundwater were higher because surface flows were much larger.

The impact of ash pond leachates and overflows on overall radionuclide levels in surface waters has not been extensively studied. Analyses to date from monitoring wells downslope from the Poplar River plant in southern Saskatchewan indicates gradually increasing uranium levels, however, this trend has been attributed to analytical error to date (PRCMA, 1981). Measurement of radionuclide levels in surface waters receiving leachate from one Iowa power plant ash pond revealed the the ash pond water had lower concentrations than water upgradient of the ponds, therefore, percolation of ash pond water appeared to have diluted normal background concentrations (Styron et al., 1981). Sediments, however, are often the primary source of radionuclides to aquatic biota and measurement of radionuclide levels in water only, may not give an adquate basis for estimation of potential bioaccumulation in systems receiving ash pond runoff or leachate. Unfortunately, no studies of sediment radionuclide levels from ash contacted wastewaters or levels in aquatic food chains were found.

In summary, the reports in the literature of measurements of radionuclides in coal-fired power plant effluents indicate the potential for bioaccumulation in food chains. The few studies of radionuclide uptake by biota in the vicinity of power plants, however, do not provide a sufficient basis from which to predict the magnitude of the problem. Further comparative studies of the movement and uptake of radionuclides in critical terrestrial and aquatic food chains near coal-fired plants in different geographic area, utilizing different types of coal, under different climatic, soil and water quality conditions, are still required.

2.3 Radioactivity in Coals, Ashes and Wastewater from Coal-fired Generating Stations

This section is based on an examination of the existing North American literature of radionuclide emissions during the coal fuel cycle including; the radionuclide content of coals, the release of radionuclides from coal storage piles, radionuclide emissions during combustion, and radionuclide releases from ash disposal sites.

Radioactivity in coal is derived from the naturally occurring radioisotopes, ^{238}U, ^{232}Th, their daughter products, and ^{40}K. Uranium tends to associate with the organic constituents of the coal, whereas, thorium and potassium tend to concentrate in the inorganic fraction (Breger et al., 1955; Beck et al., 1979).

These radioactive substances are thought to be incorporated into coal by their presence in the original peat beds or as a result of deposition from percolating groundwater containing radionuclides that have been leached from surrounding rock and soil (Breger et al., 1955). The highest uranium concentrations have usually been found at the top of the coal seams, and the highest thorium and potassium values at the top and bottom. These distributions appear to indicate the effect of leaching and intrusion of the trace elements from high concentrations in over- and underburdens (Beck et al., 1979).

The coal seam concentration of any radionuclide in the uranium and thorium decay series depends in part on its specific activity and that of its parent. The majority of the studies to date have assumed that secular equilibrium exists in coal deposits among members of both the ^{238}U and ^{232}Th decay series (Beck et al., 1979; Coles et al., 1978; Muller and Bagg, 1980). The basis for these assumptions appears to be the great age of geological deposits (Greening, 1981). The activities and concentrations of the daughters are commonly estimated from the measurement of only natural uranium and thorium. In contrast, Styron and Robinson (1977) actually found disequilibrium in the uranium decay chain for some western U.S. coals. In these cases radioactivity estimates for daughters based solely on uranium measurements would underestimate the total radionuclide content since $^{210}Po/^{238}U$ varied from 1.4 to 12.6 as the grade of coal declined. It was suggested that these enhancements may have occurred when large quantities of ^{222}Rn diffused from adjacent uraniferous rocks into lower activity coal seams with subsequent trapping of the particulate decay products in the coal. Elevated ^{210}Po levels, however, were not expected to be typical for most coals (Beck et al., 1979).

2.3.1 Radionuclides in Coal.

U.S. Coals. The results of several studies on the radionuclide content of U.S. coals are presented in Table 6. Beck et al. (1979) compiled the most comprehensive data

TABLE 6 CONCENTRATIONS AND ACTIVITIES OF ^{238}U, ^{232}TH and ^{40}K in U.S. COALS

^{238}U		^{232}Th		^{40}K		Coal Source and Rank	
Conc. (mg/kg)	Activity (Bq/kg)	Conc. (mg/kg)	Activity (Bq/kg)	Conc. (mg/kg)	Activity (Bq/kg)	A-Anthracite B-Bituminous S-Sub-bituminous L-Lignite	Reference
1.7	(22.2)	4.5	(18.5)	0.20	(51.8)	≈ 1000 samples from different U.S. regions	Beck et al. (1979)
1.5	(18.9)	5.4	(21.8)	0.28	(71.0)	Pennsylvania-A	Swanson et al. (1976)
1.4	(17.8)	4.9	(20.0)	0.27	(68.1)	Appalachian-B	Swanson et al. (1976)
3.3	(41.4)	5.2	(21.1)	0.19	(47.4)	Midwest-B	Swanson et al. (1976)
1.2	(15.2)	4.4	(17.8)	0.14	(35.5)	Alaska-S	Swanson et al. (1976)
3.2	(40.3)	8.3	(33.7)	0.35	(88.8)	Gulf Coast-L	Swanson et al. (1976)
1.1	(13.7)	2.0	(8.1)	0.13	(32.6)	Appalachian-B	Lee et al. (1977)
2.2	(27.8)	2.1	(8.5)	0.18	(45.1)	W. Kentucky-B	Lee et al. (1977)
0.7	(8.9)	1.6	(6.7)	0.030	(7.4)	Utah-B	Lee et al. (1977)
0.7	(8.9)	1.9	(7.8)	0.12	(30.0)	Wyoming-S	Lee et al. (1977)
1.2	(15.2)	4.8	(19.6)	0.042	(10.4)	N. Mexico-S	Lee et al. (1977)
0.7	8.9	1.6*	6.3*	0.10	27.0	Western Plant**	Coles et al. (1978)
2.6	31.5	5.0*	20.4*	0.20	51.8	Western Plant***	Coles et al. (1978)
(2.7)	33.3	(3.6)	14.8			6 U.S. Plants	Wagner et al. (1979)
(0.9)	11.1					coal from 19 active Western U.S. mines	Styron et al. (1981a)
(2.3)	29.2	(5.0)	20.4			Western U.S. mines	Styron et al. (1981b)
(2.1)	25.9	(2.6)	10.7			samples from coal mines in different regions	Kruger and Johnson (1978)
				(0.37)	92.5	Illinois-B	Barber and Giorgio (1976)
				(0.10)	25.9	Montana-S	Barber and Giorgio (1976)
				(0.32)	81.4	N. Dakota-L	Barber and Giorgio (1976)

Note:
* ^{228}Ra
** Low Sulphur, Low Ash
*** Low Sulphur, High Ash
( ) Calculated values

of radionuclide concentrations for a wide range of U.S. coals. The survey included data from three researchers on almost 1000 samples obtained directly from mines providing most of the coal used in the United States today (Swanson et al., 1976; Gluskoter et al., 1977, Farmer et al., 1977).

A summary of the data is presented in Table 7.

TABLE 7 AVERAGE CONCENTRATIONS AND ACTIVITIES OF RADIONUCLIDES IN U.S. COALS (Beck et al., 1979)

Radionuclide	Concentration Range (mg/kg)	Average Concentration (mg/kg)	Calculated Activity (Bq/kg)	Calculated Concentration from Measured Activity (mg/kg)
^{238}U	0.2 to 25.2	1.7	22.2	1.6
^{232}Th	0.62 to 79	4.5	18.5	4.4
^{40}K	0.01 to 2.83	0.20	51.8	0.40

Table 7 shows that the direct measurements of radioactivity in U.S. coals when converted to concentration, compares well with the actual measurements of concentration. The conversion from concentration to activity involves the following factors:

1 mg/kg Th = 4.07 Bq/kg ^{232}Th

1 mg/kg U = 12.58 Bq/kg ^{238}U

1%K = 296 Bq/kg ^{40}K (^{40}K = K x 0.118%) (Beck et al., 1979)

The concentration ranges indicate that some coals contain quantities of radionuclides 15 to 20 times higher than the mean values. Thus, there may be a wide variation of the actual activity within the ranges at any one power plant because many plants obtain coal from different mines. Furthermore, the activity in coal from a particular mine or even one seam can vary by as much as an order of magnitude (Lee et al., 1977). Beck et al. (1979) contended that over the long lifetime of most power plants, these variations in activity would average out and tend toward the mean activity for the majority of coal resources. It should be noted, however, that as power plants and mines get older and the coal resources are depleted with time, there may be an increase in the use of lower quality coals that contain more radioactive material than higher grade coal.

It was believed that western U.S. coals were 10 to 100 times more radioactive than eastern U.S. coals (Anon., 1980) until several studies indicated that coal from both regions have a comparable radionuclide content (Beck and Miller, 1980; Styron et al., 1981a; 1981b). Some unusually high values of radioactivity in coal were explained by the presence of pockets of uraniferous coals that are known to exist in two areas of the United States. In the north-central midcontinent, high sulphur, bituminous coal with uranium concentrations of 10 to 15 mg/kg, is used principally in a few relatively small power plants in Missouri and southern Iowa. Sporadically distributed uraniferous lignite near the north-western corner of South Dakota, containing up to 100 mg/kg uranium is not commercially exploited at the moment due to its very high ash and low heat content (Styron et al., 1981a).

Figure 7, derived from the values presented in Table 6 shows the concentration of ^{238}U, ^{232}Th and ^{40}K in feed coal of various ranks. Uranium concentrations appear to be higher for bituminous and lignitic coals than sub-bituminous coals. This supports the observation that low grade bituminous and lignite coal (from the Western U.S.) contains relatively higher concentrations of radionuclides. Thorium concentrations, shown in Figure 7 and in the data of Swanson et al. (1976) (Table 6), are highest in lignites, followed by anthracite, bituminous, and sub-bituminous coals. The concentration of thorium in each study was greater than the corresponding concentration of uranium by average factors of 3.6, 2.0, 3.5, and 2.6 for anthracite, bituminous, sub-bituminous and lignite, respectively. In addition, Figure 7 shows that ^{230}U, ^{232}Th, and ^{40}K values cover the widest ranges in bituminous coals. It should be noted that more than 90 percent of the coal produced in the United States is bituminous Swanson et al. (1976). Lastly, this figure shows that coal contains much lower concentrations of the weakly radioactive ^{40}K, than ^{238}U and ^{232}Th (Murray, 1982). Although the activities of ^{40}K, shown in Table 6, are sometimes reported to be higher than the corresponding activities of ^{238}U and ^{232}Th, the primary mode of decay for ^{40}K is beta emission, whereas for ^{233}U and ^{232}Th, it is alpha emission.

Canadian Coals. Of Canada's extensive coal resources (over 100 000 million tons) about 1 percent are in the Maritimes and 99 percent are in western Canada (Morrison, 1978). Bituminous represents about 53 percent of the coal burned annually, followed by sub-bituminous (31 percent) and lignite (14 percent). Information on concentrations and activities of radionuclides in some Canadian coals is presented in Table 8.

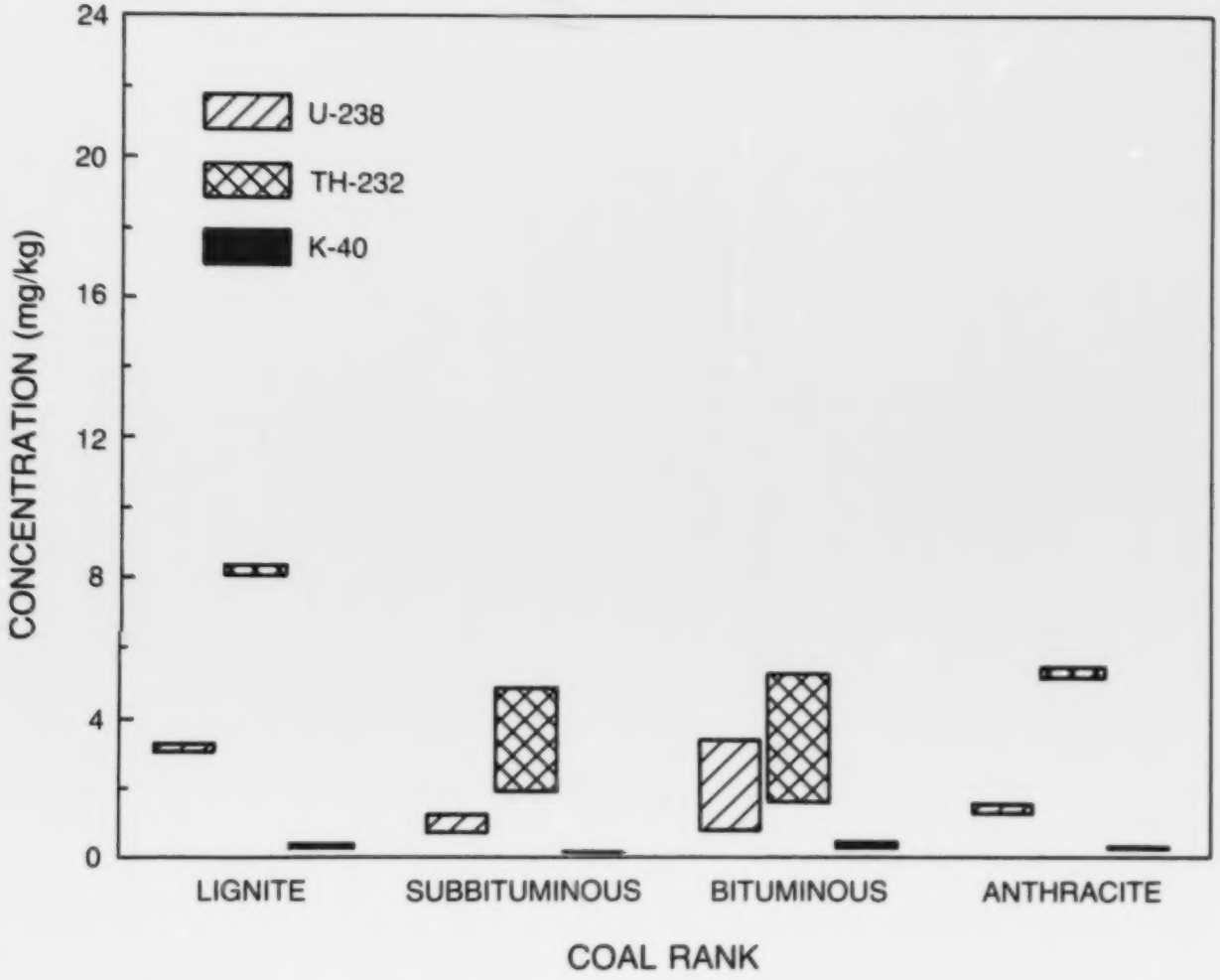


FIGURE 7 RADIONUCLIDE CONCENTRATION VERSUS COAL RANK (U.S. Coals from Table 6)

TABLE 8 CONCENTRATIONS AND ACTIVITIES OF ^{238}U, ^{232}Th, and ^{40}K IN CANADIAN COALS

^{238}U		^{232}Th		^{40}K		Coal Source and Rank	
Conc. (mg/kg)	Activity (Bq/kg)	Conc. (mg/kg)	Activity (Bq/kg)	Conc. (mg/kg)	Activity (Bq/kg)	A-Anthracite B-Bituminous S-Sub-bituminous L-Lignite	Reference
1.89	(23.7)	2.5 to 3.8	(10.4 to 15.5)			B.C. Hat Creek-S/L	Dearborn (1982)
0.6 to 1.6	(7.8 to 19.6)	1.3 to 2.0	(5.2 to 8.1)			B.C. East Kootenay-B	Dearborn (1982)
0.5 to 1.7	(6.3 to 21.8)	1.59 to 9.0	(5.9 to 36.6)			Alberta Plains-S	Dearborn (1982)
1.2 to 2.0	(14.4 to 25.5)	0.9 to 6.5	(3.7 to 26.6)			Alberta Foothills -B	Dearborn (1982)
0.8 to 2.9	(10.0 to 36.6)	1.0 to 6.6	(4.1 to 27.0)			Sask-Estevan-L	Dearborn (1982)
<0.1 to 1.0	(<1.3 to 12.2)	0.2 to 6.1	(0.7 to 24.8)			Sydney, N.S.-B	Dearborn (1982)
1.2 to 2.2	(15.5 to 27.8)	1.9 to 5.5	(7.8 to 22.6)			Pitcou & Cumberland, N.S.-B	Dearborn (1982)
1.2 to 1.6	(14.8 to 19.6)	1.1 to 3.6	(4.4 to 14.8)			N.B. Minto-B	Dearborn (1982)
2.9 to 11.0	(36.2 to 138.6)					Saskatchewan-L	MacCormack (1979)
0.78	(10.0)					Alberta-S	MacCormack (1979)
1.4	(17.8)	5.3	(21.5)			B.C. Hat Creek-S/L	B.C. Hydro (1981)
1.2	(15.2)	2.3	(9.3)			Alta-Luscar-B	Curtis (1980)
1.3	(16.3)	2.9	(11.8)			Byron Creek-B	Curtis (1980)
(1.0)	12.4	(1.9)	7.5	(0.11)	26.4	50/50 U.S. Appal & Western Canadian used at Nanticoke-B	Tracy and Prantl (1981)
0.7	(8.9)	1.4	(5.6)	0.14	(35.2)	Lakeview G.S. Eastern U.S. Coal-B	Muller and Bagg (1981)
<1 to 17	(11.1 to 214.6)					Sask-Estevan-L	Cameron and Birmingham (1970)*
1 to 22	(14.8 to 277.5)					Sask-Willowbunch -L	Cameron and Birmingham (1970)*

Note: *Original values as U_3O_8 (urano-uranic acid) converted to U by:

$$\frac{\text{wt.}U_3}{\text{wt.}\ U_3O_8} = \frac{714g}{842} = 0.85 \times U_3O_8 = {}^{238}U$$

( ) Calculated values

The analysis of coal from the Maritimes indicated concentrations of 0.1 to 1.6 mg/kg ^{238}U and 0.2 to 6.1 mg/kg ^{232}Th (Dearborn, 1982a). Blended coal in Ontario power plants (usually a 50/50 mixture of cleaned eastern U.S. and western Canadian coal) was reported to contain 0.7 to 1 mg/kg ^{238}U, and 1.4 to 1.9 mg/kg ^{232}Th -slightly less than average U.S. coals (Bagg, 1981; Tracy and Prantl, 1981). Cameron and Birmingham (1970) found relatively high concentrations of uranium (1 to 22 mg/kg) in Saskatchewan lignite. Later studies reported coal from the same region as containing 0.8 to 11.0 mg/kg ^{238}U (Dearborn, 1982a; MacCormack, 1979). Bituminous Alberta coals contained from 0.5 to 2.0 mg/kg ^{238}U (Dearborn, 1982a; B.C. Hydro and Power Auth., 1981; Curtis, 1980). Radioactivity measurements on B.C. coals by Newmarch (1953), indicated that higher ash coal samples had correspondingly larger radioactive values.

Figure 8 presents the concentrations of primordial radionuclides in Canadian coal, organized by coal rank. Uranium concentrations in lignite span a wider range and include higher values than those in bituminous and sub-bituminous coals. Although Figure 8 shows thorium as having a lower maximum concentration than uranium in lignite, the opposite is expected. This is not apparent from figure because the studies that reported the unusually high concentrations of uranium in lignite did not report the thorium content of that coal. Taking this into consideration, thorium would occur in highest concentrations in lignite followed by sub-bituminous and bituminous coals.

2.3.2 Radioactive Release Prior to Coal Combustion. Radioactivity may be released to the environment from coal storage piles in two ways. The first pathway is through runoff and leachate from coal storage areas. The second is through radon emanation from the coal pile. Available data that describes radionuclides in these two pathways is limited. Results of the few studies that have measured radionuclides from coal storage pile leachates and Ra^{222} emanation are presented in Tables 9 and 10, respectively.

U.S. Coals. Wagner et al. (1979) analyzed for the uranium series nuclides: ^{226}Ra, ^{210}Pb and ^{210}Po in bituminous and sub-bituminous coal leachates from six generating stations, two in the Illinois Basin, two in the Appalachian Region, one in the Midwest, and one from the West. The activity of ^{226}Ra was less than the detectable limit in all but one leachate source which contained 0.0185 Bq/L. Although indicated elsewhere to form the most insoluble salts, ^{210}Pb appears to be the most leachable radionuclide (Table 9). The highest ^{210}Pb activities were associated with the acidic leachates from Plants 3 and 6 which contained 0.300 Bq/L and 0.118 Bq/L. But one fairly acidic leachate, from Plant 2, showed very small ^{210}Pb activity, indicating pH may not have been the sole

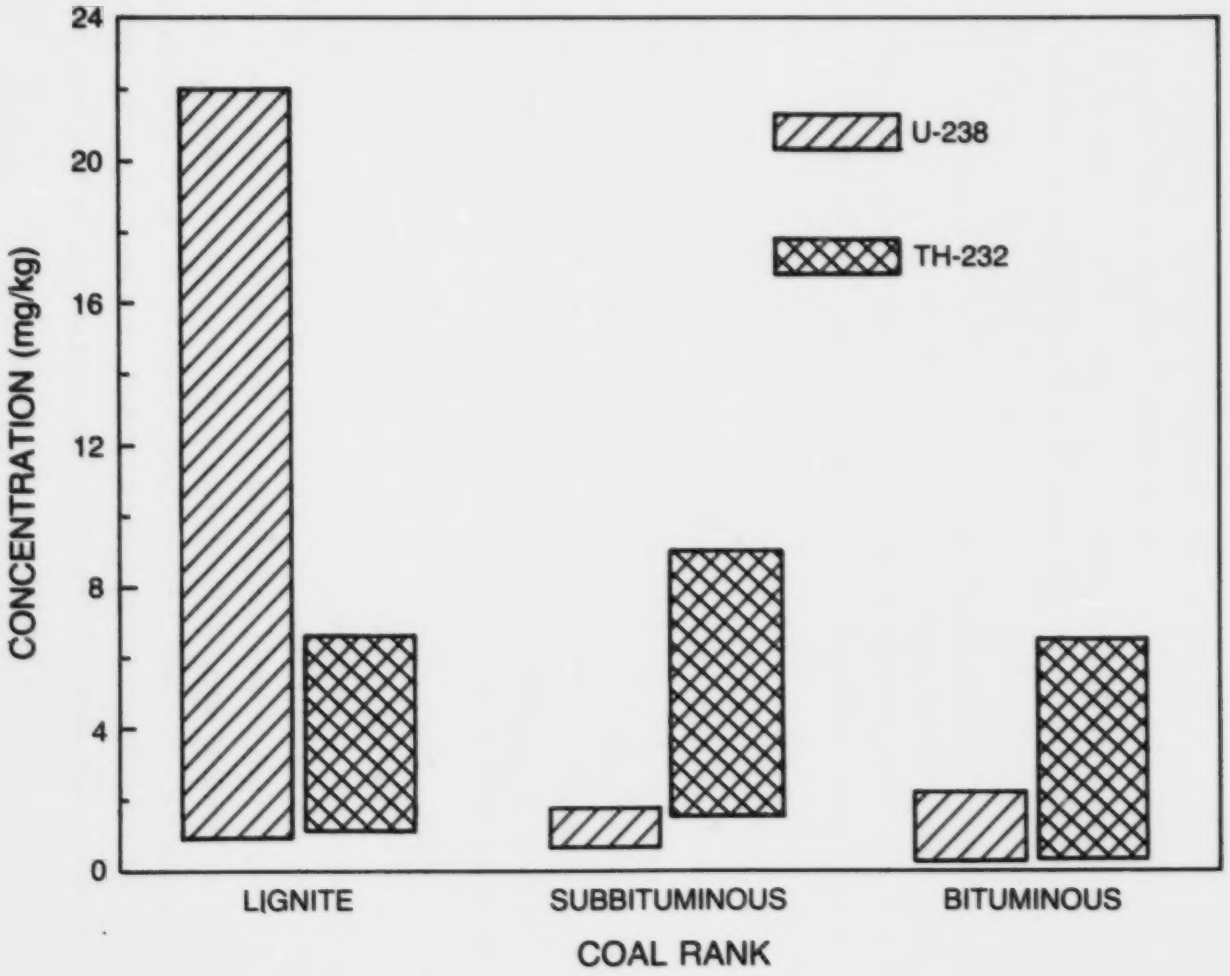


FIGURE 8 RADIONUCLIDE CONCENTRATION VERSUS COAL RANK (Canadian Coals from Table 7)

TABLE 9 RADIONUCLIDES IN COAL PILE DRAINAGE

Coal Source	Coal Type	pH	Sample* Type	Radionuclide (Bq/L) ^{238}U	^{234}U	^{230}Th	^{226}Ra	^{210}Pb	^{210}Po	^{232}Th	Reference
U.S.	Bit./Subbit.	7.8	L	-	-	-	<blank	<0.004	0.007	-	Wagner et al. (1979)
U.S.	Bit./Subbit.	3.8	L	-	-	-	<blank	<0.004	0.007	-	Wagner et al. (1979)
U.S.	Bit./Subbit.	2.9	L	-	-	-	<blank	0.300	0.011	-	Wagner et al. (1979)
U.S.	Bit./Subbit.	8.3	L	-	-	-	<blank	0.007	0.011	-	Wagner et al. (1979)
U.S.	Bit./Subbit.	7.9	L	-	-	-	<blank	<0.004	0.011	-	Wagner et al. (1979)
U.S.	Bit./Subbit.	2.7	L	-	-	-	<blank	0.118	0.022	-	Wagner et al. (1979)
U.S.	Bit./Subbit.	-	L	0.026	0.048	0.005	0.0185	0.345	-	<0.004	Styron et al. (1981b)
				(mg/L)							
Canada	Bit., High S	2.1	L & R	<0.06	-	-	-	-	-	<0.005	Dearborn (1981)
Canada	Bit., Low S	-	L & R	<0.06	-	-	-	-	-	<0.005	Dearborn (1981)
Canada/U.S.	Bit., Low S	2.8	L & R	<0.06	-	-	-	-	-	<0.005	Dearborn (1981)
Canada	Subbit., Low S	6.3	L	0.13	-	-	-	-	-	0.066	Dearborn (1981)
Canada	Subbit., Low S coal rejects, & dewatered tailings	8.3	R	<0.06	-	-	-	-	-	0.090	Dearborn (1981)

Note: * L = Leachate
R = Runoff
- = Not Available

TABLE 10 ^{222}Rn EMANATION FROM COAL PILES AND SOILS

No. of Samples	Sample Type	^{222}Ra Activity (Bq/kg)	^{222}Rn Emanation (%) *		Reference
			Mean	Range	
-	Coal	18.5	14	-	Beck et al. (1979)
-	Coal	18.5	13	-	Beck et al. (1979)
5	Soil	29.6 to 51.8	14	-	Beck et al. (1979)
6	Bituminous Coal	-	20	11 to 37	Beck and Miller (1980)
3	Lignite Coal	-	53	44 to 63	Beck and Miller (1980)

Note: *emanation (%) = ratio of escape to production

factor governing ^{210}Pb leachability. Thus a discrepancy appears to exist between the theoretical and observed chemistry of this radionuclide.

Styron et al. (1981b) also studied the mobilization of radionuclides by leaching at a western U.S. generating station. Activities of ^{234}U (0.048 Bq/L) and ^{210}Pb (0.345 Bq/L), (daughter products of ^{238}U) were significantly higher than that of ^{238}U (0.026 Bq/L) suggesting that the radionuclide decay process may cause daughters to be less bound to the solid matrix that the parent radionuclide. Radioactivity was also measured in groundwater downgradient of the coal pile. The gross beta activity, 0.348 Bq/L, was higher than that in the background wells and surface water of the Missouri River, whereas, gross alpha and ^{226}Ra activities of 0.118 Bq/L and 0.004 Bq/L, respectively, fell in between the activities found in background groundwater and river water.

Canadian Coals. A Canadian study included information on uranium and thorium concentrations in coal pile drainage from 5 different Canadian stations (Dearborn, 1982b). Uranium and thorium concentrations in the leachate samples from two maritime stations (bituminous, high sulphur coal) and an Ontario Station (cleaned bituminous, low sulphur coal) were less than the detectable limit even though the leachates had acidic pH values of 2.0 and 3.0.

The second pathway of radionuclide release from coal storage piles, ^{222}Rn emanation, was investigated in two studies and the results are shown in Table 9. Beck et

al. (1979) reported that 15 percent of the ^{222}radon emanated from two coals. This is comparable to the average radon emanation from soils. In another study, however, it was found that bituminous coals emanated 20 percent of ^{222}Rn, and lignite coals emanated 53 percent, which is significantly higher than the average for soils (Beck and Miller, 1980).

2.3.3 Radioactive Releases During Coal Combustion. Upon high temperature combustion of coal, radioactivity is released into the atmosphere in the form of gases such as radon gas or as volatilized elements or in the form of radionuclides adhering to that portion of the fly ash which escapes the emission control equipment. Escape of fly ash from ESP equipped stations is typically estimated as 0.7 percent of fly ash produced. In most studies, it is also conservatively assumed that all the radon in the coal is released from the stack.

As a result of combustion concentration on the smallest particle sizes, the radionuclides in the released particulates may be enriched relative to the input coal. In one definition the enrichment factor is defined as the ratio of the concentration of a radionuclide (X) and ^{40}K in the sample divided by the corresponding ratio in the input coal:

$$EF = \frac{(X)\ \text{Sample} \times (^{40}K)\ \text{Sample}}{(X)\ \text{Coal} \times (^{40}K)\ \text{Coal}}$$

The radionuclide concentration is most commonly normalized to ^{40}K because its concentration appears to remain more or less constant (40).

Styron et al. (1981b) concluded that secular equilibrium of the uranium decay series after ^{226}Ra is disrupted during combustion. ^{222}Rn, a decay product of ^{226}Ra, exits the stack as an inert gas following combustion; ^{210}Pb and ^{210}Po may also be emitted from the stack or adsorb to fly ash particles upon cooling as they travel up the stack. Placement of the ESP or bag particle removal device, therefore, may be important in control of release. These factors may produce the disruption.

Uranium has been found to be increasingly enriched in the fly ash with decreasing particle size, as shown in Table 11. Thorium and potassium, however, show no significant enrichment (Ondov et al., 1978; Styron, 1978).

Ondov et al. (1978) collected escaping fly ash from a western U.S. generating station, with filter and cascade impactor samples installed on a twin engin aircraft. The range of radioactivity in four samples is shown in Table 12.

TABLE 11 CONCENTRATIONS OF PRIMORDIAL RADIONUCLIDES IN POST - ESP FLY ASH (Coles et al., 1978)

Post - ESP Stack Fly Ash (mmd)**	Concentration		
	^{238}U	^{232}Th	^{40}K
18.5 µm	16	25	8200
6.0 µm	20	31	8600
3.7 µm	30	36	8600
2.4 µm	36	38	8100

* Samples from a western U.S. plant burning low sulphur (0.46%), high ash (23.3%) coal; stack fly ash collected by cyclone separator mounted at outlet of ESP unit.
** mass median diameter determined by centrifugal sedimentation.

TABLE 12 ACTIVITIES OF RADIONUCLIDES IN ESCAPING FLY ASH

	^{238}U (^{234}U)	^{226}Ra	^{210}Pb	^{232}Th (^{228}Th)	^{228}Ra	^{40}K
Activity (Bq/kg)	200 to 444	122 to 218	159 to 629	104 to 122	100 to 155	259 to 274

The researchers noted that the values of the uranium series nuclides indicated further enrichment from ESP to post-ESP fly ash.

U.S. Generating Stations. Several studies estimated the release of radioactivity from a typical 1000 MW (e) coal-fired power plant in the U.S. Of these, the study conducted by Beck et al. (1979) appears to be based on the most realistic assumptions, and incorporates the information from other investigators as well as from their own study. Based on activities of various fly ash samples, reported in 9 different studies, and extensive enrichment data, annual radioactive emissions for two typical 1000 MW (e) plants were estimated. The first scenario was a "modern" plant meeting U.S. EPA regulations requiring particulate releases to be less than 0.045 kg/2.5 x 10^5 cal (0.1 lb/10^6 BTU) of fuel burned and the second, a "1972 reference" plant representing an older, more poorly controlled plant releasing 8 percent of the total ash content of coal burned. Enrichment factors applied for the modern plant were as follows: Uranium: 2, ^{226}Ra= 1.5, ^{210}Pb= 5, ^{210}Po= 5. All other radionuclides were assumed to be unenriched. For the 1972 reference plant only ^{210}Pb and ^{210}Po were assumed to be enriched by a

factor of 2 each. For both plants, all the radon-222 gas was assumed to be released upon combustion and escape from the stack.

The emissions of radioactivity estimated by Beck et al. (1979) for the two types of plants are shown in Table 13. Two other studies that took the enrichment effect into account to predict radioactive releases from model 1000 MW (e) plants are also shown on this table. UNSCEAR (1977) assumed EFs (as described earlier) of 5 for uranium and 10 for lead, and Lee et al. (1977) assumed only lead and potassium nuclides to be enriched by a factor of 5.

The "1972 reference" plant which may be considered a present day "worst case" situation would produce a total activity twice that from the modern plant. According to the calculations the uranium series radionuclides ^{210}Pb, ^{210}Po, and ^{222}Rn would typically contribute the largest portion of the release of radioactivity.

In any given year releases for actual plants might deviate from the activities estimated by Beck et al. (1979) (Table 13) as a result of burning coal for only part of the year, or releasing ash containing activities significantly greater or less than those assumed. Nevertheless, since power plants burn coal from a variety of mines over their lifetime, the values in this table were expected to be fairly representative of long-term average releases.

Canadian Generating Stations. A few studies have predicted radionuclide emissions from the stacks of various Canadian coal-fired generating stations. MacCormack (1979) divided four Saskatchewan power plants into two categories and estimated the quantities of heavy metals leaving them. The two categories were those newer units which used electrostatic precipitators and air preheaters (Class 1), and those older units which used only cyclones for fly ash removal (Class 2). The plants burned Saskatchewan lignite containing 2.88 to 11.02 mg/kg of uranium. Assuming 0.7 percent escape of fly ash from the ESP equipped plants, the radionuclide releases were calculated to be 57 to 119 kg/yr volatilized uranium and 35 to 149 kg/yr of uranium released with escaping fly ash from an ESP equipped 300 MW (e) unit at Poplar River Generating Station. It was estimated that 53 to 201 kg/yr of uranium would leave the plant with the fly ash from the cyclone equipped units 300 MW (e) Boundary Dam Generating Station.

Based on 12.9 percent escape of fly ash from Class 2 plants, it was estimated that 1139 to 4468 kg/yr of uranium volatilized, and 33 to 123 kg/yr of uranium was released with escaping fly ash from the 70 MW (e) Estevan Generating Station. It was calculated that 6920 to 26 543 kg/yr of uranium volatilized, and 193 to 753 kg/yr of

TABLE 13 ESTIMATES OF ANNUAL RADIONUCLIDE RELEASES FROM 1000 MW (e) U.S. COAL-FIRED POWER PLANTS (Beck et al., 1979)

Fraction of Fly Ash Released (%)	Total Fly Ash Released (kg/yr)	Activity Released (Bq/yr x 10^7)											Reference
		^{238}U	^{234}U	^{230}Th	^{226}Ra	^{232}Th	^{228}Th	^{228}Ra	^{210}Pb	^{210}Po	^{40}K	^{222}Rn	
0.5	1.1 to 4.9 x 10^6	15 to 41	15 to 41	15 to 41	15 to 41	12 to 37	12 to 37	12 to 37	67 to 200	67 to 200	67 to 200	296 to 9620	Lee et al. (1977)*
~3 to 5	1 x 10^7	185	185	37	37	37	37	37	370	370	555	3700	UNSCEAR (1971)
~1 to 2	3.1 x 10^6	104	104	56	78	41	41	41	259	259	115	3700 to 7400	Beck et al. (1979) Modern Plant**
~10	2.8 x 10^7	466	466	466	466	385	385	385	932	932	1036	3700 to 7400	Beck et al. (1979) 1972 Reference Plant***

Note: * range of releases for plants burning different types of coal
** ash released based on just meeting EPA Standard of 0.116/10^6 BTU, assuming 80 percent utilization factor, 35 percent thermal efficiency
*** ash released based on average releases from all U.S. plants in 1972, assuming typical 1000 MW (e) plant burns 2.7 x 10^9 kg coal/yr

uranium was released with escaping fly ash from Units 1 - 5 (582 MW(e)) at the Boundary Dam Generating Station.

A summary of other studies which estimated annual emissions of radioactivity from Canadian coal-fired power plants is presented in Table 14 (Muller and Bagg, 1980; Tracy and Prantl, 1981; B.C. Hydro and Power Auth., 1981). Although Lakeview Generating Station and the proposed Hat Creek Generating Station are plants of comparable capacity, the latter was predicted to release three times more uranium series radionuclides. This may be partly a result of the type of coal burned at each plant, (cleaned bituminous at Lakeview Generating Station - low-grade sub-bituminous at Hat Creek Generating Station) and also influenced by the efficiency of the pollution control equipment employed at each plant. The Lakeview Generating Station was assumed to release 0.7 percent of fly ash per year, whereas the Hat Creek study assumed that 1 percent of the uranium and 0.11 percent of the thorium in the coal was emitted to the atmosphere via the stack.

Tracy and Prantl (1981) measured the radionuclide concentrations in fly ash from Nanticoke Generating Station, burning a 50/50 mixture of cleaned Eastern U.S. and Western Canadian coals. The results were, 92 Bq/kg (7.3 mg/kg) of U-series isotopes, 58 Bq/kg (14.3 mg/kg) of Th-series isotopes and 204 Bq/kg (0.81 mg/kg) of ^{40}K. Based on these concentrations in the fly ash and the plants annual particulate emission, the release of activity from the 4000 MW(e) plant was estimated to be significantly less than from either Lakeview Generating Station or the proposed Hat Creek Generating Station, perhaps, in part, owing to the modern control equipment at Nanticoke which includes ESPs with a rated efficiency of 99.5 percent.

The results of studies of two operating and one planned generating stations suggested that uranium series isotopes constituted the main portion of the total activity released from the coal-fired generating stations. ^{210}Pb, ^{210}Po and ^{222}Rn were believed to be the primary contributors.

2.3.4 Radionuclide Releases Resulting From the Solid Wastes of Coal Combustion. Radioactive isotopes in the solid wastes of coal combustion can be released to the environment via two major pathways. The first pathway is the leachate from ash ponds or leachate/runoff from ash pile, and the second is the emanation of radon gas from ash disposal sites or dusting.

TABLE 14 ESTIMATES OF ANNUAL RADIONUCLIDE RELEASES FROM CANADIAN COAL-FIRED POWER PLANTS

Fraction Fly Ash Released per Year (%)	Total Fly Ash Released (kg/yr)	Activity Released (Bq/yr x 10^7)										• Power Plant - Capacity - Coal Type	F.F. (assumed)	Reference
		^{238}U	^{234}U	^{230}Th	^{226}Ra	^{232}Th	^{228}Th	^{228}Ra	^{210}Pb	^{210}Po	^{40}K	^{222}Rn			
0.7	-	99	99	50	75	32	32	48	248	248	-	10360	• Lakeview - 2400 MW(e) - (F) Lig., Bit.	U: 2.1 Ra: 1.5 Po: 5.0 Pb: 5.0	Muller and Pagg (1980)•
0.5	1.33×10^6	14 (a)	14 (a)	14 (a)	14 (a)	9 (a)	9 (a)	9 (a)	41 (c)	41 (c)	32 (a)	4725 (b)	• Nanticoke - 4000 MW(e) - 50/50 (e) Lig. & (W) Canadian Bit.	Pb: 5.0 Po: 5.0	Tracy and Prantl (1981)••
-	-	333	333	166	252	27	27	41	851	851	-	32296	• Hat Creek (proposed) - 2000 MW(e) - Subbit.	U: 2.0 Ra: 1.5 Po: 5.0 Pb: 5.0	B.C. Hydro and Power Auth. (1981)•••

Additional Assumptions:

• Station Efficiency: 35%, heating value of coal: 27 GJ/MT, mineral content: 8.5%; annual release rate of U nat. and Th nat. is 79 kg each

•• (a) based on concentration in fly ash and annual particulate emission of 1.929×10^6 kg
(b) based on concentration in feed coal, and annual coal consumption of 3.8×10^9 kg
(c) as in (a), except EF's assumed for Pb and Po

••• 1. continuous operation at the peak coal consumption rate of 40 482 t/d
2. 23.6% moisture content in the "as received" coal
3. 10% of the uranium and 0.11% of the thorium in the coal is emitted to the atmosphere via the stack

U.S. Generating Stations. Results of radioactivity measurements of ash samples from various eastern and western U.S. power plants, as reported in 11 different studies, were compiled and the averages are presented in Table 15 (Beck et al., 1979).

TABLE 15 RADIOACTIVITY IN ASH SAMPLES COLLECTED IN POWER PLANTS IN THE UNITED STATES

	Radionuclide Activity (Bq/kg)						
Sample	^{238}U (^{234}U)	^{226}Ra	^{210}Pb	^{210}Po	^{232}Th (^{228}Th)	^{238}Ra	^{40}K
Fly Ash	107.3	92.5	166.5	196.1	85.1	74.0	466.2
Bottom Ash	81.4	62.9	74.0	185.0	62.9	66.6	314.5

The results indicate an enrichment of fly ash relative to bottom ash due to the tendency for some of the more volatile radionuclides to preferentially recondense on smaller particles. Within these results, a study that analyzed 6 lignite and 5 bituminous coal ashes, each from a different power plant, reported no significant differences in activity between the two coal types. Furthermore, in comparing the activities with those for typical soil ^{238}U: 26 Bq/kg, ^{232}Th: 26 Bq/kg and ^{40}K: 370 Bq/kg, it was clear that ash has radioactivity several times that of average soil (Beck and Miller, 1980).

Styron et al. (1981b) performed leaching experiments on ash stored in an ash pond at the Neal Generating Station, Iowa which burns bituminous/sub-bituminous coal, as well as on fly ash containing a relatively large amount of uncombusted material from a Colorado plant.

Data in Table 16 indicate the limited solubility of radionuclides bound in fly ash particles.

The second pathway of radionuclide escape into the environment is the emanation of ^{222}Rn from ash disposal areas, a potential problem which has been addressed in a few studies (Lee, 1977; Beck and Miller, 1980; Styron et al., 1981b). In 11 samples, the measured radon emanation, for fly ash, bottom ash and slag averaged less than 2 percent of the total present in the ashes (Beck and Miller, 1980). Radon emanation from the Neal Station 500 000 m^2 ash pile was calculated to be 5.25×10^{10} Bq/yr.

Lee et al. (1977) estimated the radon generated from a 30 year old ash pile of a typical 1000 MW(e) plant (at a depth of 40 feet with a density of 60 lb/ft^3) would be

TABLE 16 RADIONUCLIDES LEACHED FROM FLY ASH

	Radionuclide			
	^{238}U	^{234}U	^{232}Th	^{210}Pb
Activity (Bq/L)	0.0003 to 0.0014	0.0005 to 0.0011	0.002 to 0.0007	0.0185 to 0.0370
Percentage Leached	0.001 to 0.003	0.0019 to 0.0025	0.0015 to 0.001	0.04 to 0.07

3.9×10^5 Bq/m^2/d. Assuming 1 percent emanation, 0.039×10^5 Bq/m^2/d would result. This estimated value is three times that for average soil (0.014×10^5 Bq/m^2/d) (Lee et al., 1977).

A further possible pathway of radiation release from ash storage areas could be the suspension and dispersion of ash itself. This was explored by Styron et al. (1981b), for the ash pile at the Neal Station. Although they concluded that this pathway was not a significant one at that time, weathering effects would eventually increase the releases from this source.

Canadian Generating Stations. Radioactivity in ash samples from Ontario Hydro's Nanticoke Generating Station, which burns a mixture of Canadian and U.S. bituminous coals, was found to be 2 to 4 times as high as local soils (Tracy and Prantl, 1981). As shown in Table 17 the activities in the fly ash were comparable to those in the bottom ash.

TABLE 17 RADIOACTIVITY IN ASH FROM THE NANTICOKE GENERATING STATION

	Radionuclide Activity (Bq/kg)		
Sample Type	U - Series	Th - Series	^{40}K
Fly Ash	92	58	204
Bottom Ash	91	61	245

Leaching of radionuclides from the ash at the Nanticoke station was studied by performing laboratory solubility tests on samples from the ash storage lagoon. The results indicated a slight leachability of uranium at 1.4 to 2.0 µg/L; ^{226}Ra and ^{210}Pb was marginally detectable at 0.10 ± 0.04 Bq/L (Tracy and Prantl, 1981).

Emanation of ^{222}Rn from an ash pile at the proposed Hat Creek station was estimated based on the measured concentration of ^{226}Ra in the fly ash from the Battle River Generating Station test run of Hat Creek coal. Ash pile accumulation of 35 years and a radon-222 emanation of 1 percent were assumed. The resulting emanation was calculated to be 0.14×10^5 Bq/m^2/d, which is an order of magnitude higher than that reported for average soils (0.014×10^5 Bq/m^2/d) (Lee et al., 1977).

2.4 Summary

In the literature, radionuclide concentrations in both U.S. and Canadian coals were indicated to vary over a wide range. A set of averages for U.S. coals of ^{238}U: 1.7 mg/kg (22.2 Bq/kg), ^{232}Th: 4.5 mg/kg (18.5 Bq/kg) and ^{40}K: 0.20 mg/kg (51.8 Bq/kg) were lower than the corresponding concentrations in average soil of 2.0, 6.0 and 1.5 mg/kg (Wagner et al., 1979). Coals fired in Ontario power plants, commonly a 50/50 mixture of eastern U.S. and western Canadian cleaned coals, contained 0.7 to 1 mg/kg ^{238}U and 1.4 to 1.9 mg/kg ^{232}Th. Saskatchewan lignite had a relatively wide concentration range of 0.8 to 22 mg/kg ^{238}U. Both B.C. and Alberta coals had comparable concentration of ^{238}U of approximately 0.5 to 2 mg/kg. The radionuclide content of both U.S. and Canadian coals appeared to vary with rank; uranium had a higher upper limit and spanned a wider range of values for lignite and bituminous coals compared to sub-bituminous coals. Comprehensive analytical data on radionuclides in Canadian coals, however, was lacking. In particular, the uranium and thorium decay products had not yet been thoroughly quantified.

Radioactivity released during coal combustion consisted primarily of escaping fly ash and ^{222}radon gas. Secular equilibrium of the uranium decay series after ^{226}Ra appeared to be particularly susceptible to disruption. Uranium series radionuclides, especially ^{210}Pb and ^{210}Po were reported to be enriched on the smaller size ash particles. Enrichment factors which were normalized using ^{40}K concentrations, however, were used to determine these factors. This in turn was based on the assumption that the ^{40}K concentrations remained constant in the coal and sample. Although these assumptions are often made, they have rarely been verified through analysis and reported in the literature.

The amount of radioactivity released appears to depend on the method of operation of each power plant. The type of coal used, rank, washed and unwashed; the furnace type, pulverized or cyclone fired; and pollution control equipment, baghouse, hot or cold side ESP, could each affect the radionuclide emissions. These factors, however, have not always been recognized in the studies published to date.

Limited information was available on the release of radioactivity in leachates and ^{222}Rn emanation from coal storage piles and ash disposal areas. Although ESP fly ash often contained activities several times those of average soils, it generally emanated little radon (approximately 1 percent). Radionuclide concentrations in ash leachates appeared to be lower than in coal leachates and ^{222}Ra emanation from ash appeared to be much less than from coal.

Previous studies concerned with radionuclide emissions from coal-fired generating stations have often used estimated values based on assumptions of secular equilibrium and constant concentration to arrive at their conclusions. These assumptions have not always been born out in the limited testing which has been performed to date. More measurements of the radioactive substances in coal, ash and leachates at generating stations are necessary for a better understanding of the situation. In the future, as coal resources become depleted, lower rank coal, possibly containing higher levels of radioactivity may have to be used. An increase in the amount of radionuclides entering coal-fired stations is to be expected, therefore, and with it there is an increasing need for a better understanding of these pathways.

3 SAMPLING PROGRAM AND ANALYTICAL METHODS

In this section the six generating stations where sampling took place during the field program for this study are described and details on the sampling procedure at each site are provided. The analytical procedures used for the quantification of chemical and radiochemical analyses are also discussed.

3.1 Sampling Program

Six generating stations representing a variety of generating capacities, coal ranks, ash disposal systems and operating modes were selected for the on site sampling program. The pertinent characteristics of each site sampled are summarized in Table 18.

At each site at least six samples of coal, fly ash, bottom ash, ash system blowdown and coal pile runoff were collected for chemical and radiochemical analyses. Table 19 shows the locations of the sites and dates when samples were obtained.

Liquid samples were preserved using methods currently recommended by the U.S. Environmental Protection Agency (Anon., 1976). Samples to be analyzed for radionuclides were preserved in the field by the addition of nitric acid to produce a pH of less than 2 (Smithson, pers. comm., 1982).

Trenton Generating Station. The Trenton Generating Station is located near Trenton, Nova Scotia, has a generating capacity of 150 MW and burns high sulphur bituminous coal. A combined hydraulic wet sluice system is used to transport fly and bottom ashes to a lagoon for ultimate disposal at this station.

At the time of sampling, the majority of coal in storage was from the Devco Prince Mine with lesser amounts from Evans and Drummond mines and reclaimed coal from the Novaco mine. Coal samples 1, 2 and 3 were from the Devco coal while samples 4, 5 and 6 were from the Evans coal which was on site. Fly ash samples were collected from the hoppers below the electrostatic precipitators. The bottom ash samples were collected in the boiler bottom area before sluicing.

Due to winter conditions, the overflow from the combined ash disposal lagoon was not accessible. Samples of the combined ash sluice water were taken at the point where it entered the lagoon. These samples would represent the worst case for the lagoon and would likely contain higher concentrations than the lagoon overflow. Six samples of coal pile runoff were collected following a rainstorm in April.

TABLE 18 CHARACTERISTICS OF STATIONS SAMPLED DURING THE FIELD PROGRAM

		Coal						Ash System		
Generating Station	Capacity (MW)	Rank	On-site Storage (Tonnes)	Heating Value (MJ/kg)	Moisture (%)	Ash (%)	Sulphur (%)	Fly Ash	Bottom Ash	Blowdown (L/S)
Trenton	150	B	3.2×10^4	25	11.3	13.8	3.5	ESP; Combined; OT	OT; Combined	Unknown
Dalhousie	212	B	6.9×10^4	23.3	9	9	6	ESP; Dry	Recirc; Hydrobin	5.3
Lambton	2000	B	2.3×10^6	29.5	7.2	8.4	2.3	ESP; Dry	OT; Lagoon	Unknown
Boundary Dam	882	L	N/A	15.7	33.3	9.5	0.4	ESP; Combined; OT	OT; Combined	Unknown
Sundance	2100	SB	$9.0 \times 10^{5+}$	22.2	4.4	18.5	0.3	ESP; Dry	Recirc; Hydrobin	Unknown
Milner	150	R/SB	2.8×10^6	21.5	7.2	40.2	0.4	BH; Dry	Recirc; Hydrobin	Unknown

Note: B denotes bituminous; SB-sub-bituminous; L-lignite; R-coal rejects
ESP electrostatic precipitator; BH-Baghouse; OT-once-through; Recirc.-recirculating
+ includes live, dead and run of mine storage
• heating value of coal only
N/A Not available

TABLE 19 SUMMARY OF SAMPLING PROGRAM

Generating Station	Location	Date Sampled (1982)				
		Coal	Fly Ash	Bottom Ash	Ash System Overflow	Coal Pile Runoff
Trenton	Trenton, N.S.	Feb. 2	Feb. 2	Feb. 2	Feb. 2	April 14
Dalhousie	Darlington, N.B.	Jan. 10/ Mar. 3	Jan. 10*/ Mar. 3	Jan. 10/ Mar. 3	Jan. 10/ Mar. 3	May 19
Lambton	Courtright, Ont.	Feb. 8	Feb. 8	Feb. 8	Feb. 8	June 5
Boundary Dam	Estevan, Sask.	Jan. 24	Jan. 24	Jan. 24	Jan. 24	May 25
Sundance	Wabamun, Alta.	Feb. 16	Feb. 16	Feb. 16	Feb. 16	July 13
Milner	Grande Cache, Alta.	Feb. 18	Feb. 18	Feb. 18	Feb. 18	July 29

Note: *pyrites also sampled at Dalhousie, January 10, 1982

Dalhousie Generating Station. The Dalhousie Generating Station has a generating capacity of 212 MW, burns high sulphur bituminous coal and is located near Darlington, New Brunswick. At this station, a dry fly ash handling system is used while a recirculating hydrobin based wet system is utilized for bottom ash transport.

The six coal samples were taken at different locations in the on-site coal storage area. Fly ash samples were collected from below the electrostatic precipitators. Bottom ash samples were taken from the bottom ash hauling trucks. Samples of pyrites were taken from the pyrite storage tank in the powerhouse.

The samples of ash system blowdown were taken from the surge tank overflow of the recirculating bottom ash system. Coal pile runoff samples were collected sequentially during a brief rainstorm from the coal pile runoff flow measurement weir.

Lambton Generating Station. The Lambton Generating Station near Courtwright, Ontario has a generating capacity of 2000 MW and burns medium sulphur bituminous coal. Fly ash is handled dry and truck transported to the on site disposal area. Bottom ash is hydraulically sluiced to settling lagoons and then the ash is truck transported to the same ash disposal site.

The six coal samples for this site are multiple subsamples of a monthly average sample which is continually collected by the station staff. Fly ash samples were

collected from the hoppers below the electrostatic precipitators while bottom ash samples were collected from ash hauling trucks.

The ash system blowdown samples were collected from the ash settling tanks south of the station powerhouse. Coal pile runoff samples were collected on June 5 following a period of heavy rain. Samples 1 and 2 were collected from the east side of the coal storage pile while samples 3 and 4 were from the west side and samples 5 and 6 were from water puddles on the coal pile itself.

Boundary Dam Generating Station. The Boundary Dam Generating Station located near Estevan, Saskatchewan has six operating units each with different equipment configurations. Where possible, sampling was centered around unit 6 which has a generating capacity of 300 MW. Lignite coal which is supplied from a nearby strip mine is burned at the plant. The station uses a once through combined fly and bottom ash wet sluice system.

Coal samples were collected from the feeder belts to the coal storage bins. Fly ash samples were collected from hoppers below the electrostatic precipitates. Bottom ash samples were collected in the boiler bottom area following contact with the ash sluice water.

The ash system blowdown samples were collected from ash lagoon overflow discharge canal. Coal pile runoff samples were collected from the on-site coal storage pile following a period of heavy rain.

Sundance Generating Station. The Sundance Station is located near Wabamum, Alberta and has a generating capacity of 2100 MW. This station burns low sulphur sub-bituminous coal which is strip mined nearby. Dry fly ash handling is used while bottom ash is transported using a recirculating hydrobin system. Bottom ash is removed from the site using mine trucks.

Coal samples were collected from the coal feeder belts. Fly ash samples were collected from below the electrostatic precipitators while bottom ash was collected in the boiler bottom area following contact with the ash sluice water.

During the site visit to this station, the recirculating bottom ash system was operating without a blowdown. The samples designated as ash system blowdown were taken from the recirculated bottom ash sluice water line. Coal pile runoff samples were collected from around the coal storage pile following a heavy rainstorm.

Milner Generating Station. The Milner Generating Station is located near Grande Cache, Alberta and has a generating capacity of 150 MW. This station burns a

mixture of sub-bituminous coal and coal processing plant rejects both from a nearby mine and processing plant. Fly ash is collected using a baghouse and is dry hauled to the mine site for disposal. A recirculating hydrobin ash system is used to transport the bottom ash.

The coal samples for this site were collected from the coal feeder belts in the powerhouse. The flyash samples were collected from the hoppers below the baghouse. The bottom ash samples were collected from the top of a decanted hydrobin.

The ash system overflow was not accessible for sampling at this station. The samples were, however, taken from the recirculated bottom ash sluice water line as it returned to the boiler area. Coal pile runoff samples were collected from a drainage ditch below the coal storage pile.

3.2 Analytical Procedures

All samples collected were subjected to a number of chemical and radiochemical analytical procedures which are described in this section. Due to the extensive analyses performed and the nature of the samples, emphasis has been placed on the description of the radiochemical analytical procedures used during this study. The ash system blowdown and coal pile runoff samples were also analyzed for non-radioactive substances.

Chemical Characterization. The non-metal parameters were obtained using wet chemical techniques as described in Standard Methods (Franson, 1980). Total dissolved solids were quantified using the evaporative procedure from the same source. The majority of metals were determined using inductively coupled argon plasma (ICAP) spectroscopy following an appropriate digestion procedure. All of these determinations are expressed as total metal concentrations.

Radionuclide Measurements. The choice of the analytical methods to determine radioactive isotopes is based on considerations of sensitivity, selectivity, cost, nature of the sample and availability of necessary instrumentation. In general, radiochemical separations followed by low-background alpha or beta counting are the best in terms of sensitivity and selectivity but are usually the most costly. Methods of this type are usually specific to a single isotope, although, procedures can determine several isotopes simultaneously. These are usually alpha spectroscopic measurements for groups of isotopes such as thorium isotopes, uranium isotopes or transuranic isotopes. Preparation of the final sample for alpha spectroscopic measurement is very critical. Until a few years ago the normal preparation technique was electrodeposition of the chemically

isolated isotopes onto a suitable metal surface. This technique often leads to very erratic recoveries and requires a great deal of skill and control by the analyst. Recently, techniques have been developed for co-precipitation of the isotopes of interest with micro amounts of a suitable carrier (Zimmerman and Armstrong, 1975; Sill and Williams, 1981). Although resolution by this method is not as good as by electrodeposition the reliability of results is usually better. Since alpha spectroscopy is the only means of measuring all three alpha emitting thorium isotopes (^{232}thorium, ^{230}thorium, and ^{228}thorium), its choice for this group was mandatory.

The main advantage of gamma spectroscopy is that it can be used to determine several isotopes simultaneously. Unlike alpha and beta emissions which are severely if not completely absorbed within the bulk sample, gamma rays penetrate great thicknesses of most materials. Consequently, sample preparation for gamma spectroscopy is greatly simplified. As long as the sample can be presented to the detector in a constant or controlled geometry no preparations such as fusion, acid digestion, or ashing are required. The main limitations are a lack of sensitivity (as compared to radiochemical procedures), the fact that a number of the naturally occurring radioisotopes do not emit gamma rays and the extremely high cost of gamma spectroscopy systems ($30 000 to $100 000).

When a nuclear reactor is available, there are two other analytical techniques that can be used for the determination of ^{238}uranium, ^{235}uranium and ^{238}thorium. These methods measure the mass of the isotopes rather than their intrinsic radioactivity. The first technique is instrumental neutron activation analysis. It can be used to determine nanogram levels of ^{238}uranium and ^{232}thorium. Because of their extremely low mass levels, the daughter radionuclides of these two elements cannot be determined by this method. The second technique is delayed neutron counting for ^{235}uranium. Since ^{235}uranium normally constitutes 0.72 percent of natural uranium, its measurement is an indirect measure of the ^{238}uranium present. These nuclear activation methods are sensitive with a detection limit of 20 to 100 nanograms, very little sample preparation is required and the methods are quick and cost effective. The major limitation in their application is the requirement of a nuclear reactor.

In summary, alpha spectroscopy was chosen for the simultaneous determination of ^{232}thorium, ^{230}thorium, and ^{228}thorium. Gamma spectroscopy was used to measure ^{234}thorium, ^{226}radium, ^{214}lead, ^{214}bismuth, and ^{210}polonium in the uranium series and ^{212}lead and ^{208}thalium in the thorium series. Neutron activation was used for the determination of ^{238}uranium and ^{232}thorium. In some cases, delayed neutron

counting was used to confirm the foregoing ^{238}uranium measurements. Alpha spectroscopy and gamma spectroscopy are techniques that measure actual radioactivity, from which, mass can be calculated knowing the specific activity of the individual isotopes. In contrast, neutron activation is a measure of the mass of isotope present. From this, the activity can be calculated.

Alpha Spectroscopy. The method for determining the three thorium isotopes (232, 230 and 228) consisted of the following steps. Solid samples were first dried and ground. For liquid samples, a given volume was evaporated to dryness. For coal and liquid residues that contained coal fines, the sample was ashed after drying in order to destroy the organic fraction. At this stage ^{234}thorium was added as a tracer for the remainder of the procedure. These ashed materials along with the fly ash and bottom ash were dissolved by first treating with hydrofluoric and sulphuric acids to volatilize silica. The residue was then fused with potassium pyrosulphate and following this was dissolved in dilute nitric acid. For most of the samples, the dissolved fusion melt was treated to isolate the thorium isotopes using lanthanum as the carrier. The isolation procedure consists of precipitating lanthanum hydroxide, dissolving this precipitate and precipitating lanthanum fluoride and then dissolving the lanthanum fluoride followed by an extraction with thenolytrifluoroacetone in petroleum ether. The extraction selectively concentrates thorium in the organic phase. A nitric acid strip of the organic phase returns the thorium isotopes to aqueous solution from which they are precipitated using a small quantity of cerous hydroxide as carrier. The cerium-thorium hydroxide precipitate is collected on a very fine pore membrane filter and then the thorium isotopes are quantitated by alpha spectroscopy. This result is corrected for the recovery of ^{234}thorium as determined by beta counting. The thorium isolation procedure is given in CANMET Report 78-22 (Anon., 1979) and the cerium precipitation is described by Sill (Zimmerman and Armstrong, 1975).

For some of the coal pile runoff samples with high levels of suspended solids, the final ash was sufficiently high in iron and aluminum concentrations that interference and detection limit problems developed. In order to alleviate these problems, a special isolation procedure was developed involving several barium sulfate precipitations following the initial hydroxide precipitation. In solutions containing high potassium concentrations, barium sulphate is a very efficient carrier of thorium. The final barium sulphate precipitate was dissolved in a solution of ethylenediaminetetraacetic acid from which the cerous hydroxide was precipitated and treated as previously described.

The alpha spectroscopic procedure can detect as little as 0.01 Bq. For normal solid samples where one gram is analyzed, this would correspond to a detection limit of 0.01 Bq/g. The detection limit for water samples depends on the aliquot size finally analyzed and would normally be a maximum of 0.01 Bq/litre. The precision for levels above 0.3 Bq is approximately $\pm$ 7 percent (1 sigma standard deviation).

Gamma Spectroscopy. For solid samples, the dried, ground material was placed in a 500 mL marinelli beaker. The beaker lid was sealed to ensure the establishment of equilibrium between ^{222}radon and the ^{226}radium in the sample. The sealed beaker was held for 30 days (which produces 99.6 percent of equilibrium) then the gamma spectroscopy measurement was made. The marinelli beaker was placed directly on the detector (12 to 17 percent coaxial, intrinsic germanium detectors) and counted for 12 hours. These detectors were housed in a lead shield which was 10 cm thick on all sides. The gamma spectrum was analyzed on a Nuclear-Data 6600 computerized gamma spectroscopy system. The individual gamma peaks identified in this manner were compared to calibration values taking into account the volume of the marinelli beaker filled by the sample. The calibrations were prepared by filling marinelli beakers to various volumes with fly ash and bottom ash samples that had been spiked with a standard uranium-thorium ore. The spiked material was thoroughly ground and mixed before placing it in the beaker and then was sealed for 30 days before the gamma measurement was made.

For liquid samples, the residue left after evaporating the sample to dryness was placed in a 6-cm diameter petri dish (plastic) and sealed for ingrowth of radon and its daughters. Standards were prepared by placing ground rock samples containing known amounts of uranium and thorium in plastic petri dishes and sealing for 30 days before counting. The dish was placed directly on top of the detector for counting and data processing was performed as previously described. The isotopes measured by this technique, the wavelength of the gamma line and the absolute detection limit are given in Table 20.

The detection limit for each sample type depends on the amount of sample and sample geometry. In the case of ^{234}thorium the detection limit for a 1 litre sample evaporated to dryness is in the range 0.5 to 1.0 Bq/L. For solid samples, where several hundred grams of sample is used, the detection limit for ^{234}thorium is about 0.01 Bq/g (100 g sample) to about 0.005 Bq/g (500 g sample). The precision of measurement is approximately $\pm$ 5 percent (1 sigma standard deviation) for levels of activity above 10 Bq.

TABLE 20 URANIUM SERIES AND THORIUM SERIES ISOTOPES MEASURED BY GAMMA SPECTROSCOPY

Isotope	Wavelength (keV)	Detection Limit, Absolute (Bq)
Uranium Series		
^{234}Thorium	63.3, 92.5	0.5
^{226}Radium	186.2	1.2
^{214}Lead	295.2, 352.0	0.11
^{214}Bismuth	609.3	0.15
^{210}Lead	46.5	2.5
Thorium Series		
^{212}Lead	238.6	0.15
^{208}Thalium	583.1	0.10

Neutron Activation Analysis. The neutron irradation of samples containing ^{238}uranium and ^{232}thorium results in the formation of the isotopes ^{239}uranium and ^{233}thorium, respectively. The product nuclides have relatively short half-lives (^{239}U, 23.5 min., ^{233}Th, 22.2 min.) resulting in efficient activation. The location of the gamma emissions and their intensity, however, makes the direct quantitation by these two nuclides difficult. Both product isotopes decay by beta emission resulting in the production of ^{239}neptunium from ^{239}uranium, and ^{233}protactinium from ^{233}thorium. These decay product isotopes have much longer half-lives (^{239}Np, 2.35 days; ^{233}Pa, 27.0 days) which means that the samples can be allowed to decay for several days resulting in a greatly decreased background and correspondingly higher detection limits for the measured isotopes and hence the original precursors. With an irradiation of 2 x 10^{14} neutrons/cm^2 and a subsequent decay of 3 to 5 days it is possible to detect approximately 50 nanograms of uranium and 200 nanograms of thorium. The normal sample size is 0.5 to 1.0 g for solids and 50 mL of solution evaporated to dryness. These sample sizes result in detection limits of approximately 0.1 µg/g for thorium in solids and 3 µg/L for thorium in solution. The precision of the method is approximately 5 percent (1 sigma standard deviation) for levels 100 times the detection limit. There are no serious interferences in this method for either isotope.

4 ANALYTICAL RESULTS

The results of the chemical and radiochemical characterizations of the coal, coal pile runoff, ashes and ash system overflows at the six coal-fired generating stations where sampling was conducted are discussed in this section. All the results of the radionuclide determinations including the mean and standard deviation of the analytical results for the discrete samples are presented in the Appendix. The data for the six sites as the radionuclides flow through the stations from the coal to the ash systems are summarized in Figure 9 and Tables 21 to 26. The values shown in Figure 9 are expressed as concentrations although the associated activities and the conversion factors used are presented in the Appendix. These values were quantified using the procedures described in Section 3 of the report.

These data are presented in different forms in the following section in order illustrate different aspects of natural radionuclide emissions from coal-fired generating stations, to compare these empirical data with the results of other researchers and identify areas of possible environmental hazard. In order to better interpret these results and make comparisons, several important concepts previously presented are also reviewed again here.

In the three naturally occurring radioactive decay series there are ten different elements. In undisturbed primordial materials these elements exist in an equilibrium determined by the decay characteristics of each member. This is known as secular equilibrium. When such a material is exposed to environmental factors such as oxidation, reduction and water leaching or gaseous members are allowed to escape, this equilibrium may be disrupted. One of the most striking examples of radioactive disequilibrium is the presence of becquerel levels of ^{222}radon in well waters from different parts of the world and the complete absence of ^{226}radium which is the immediate parent of the radon. This phenomenon is caused by the ability of the gaseous ^{222}radon to diffuse from ^{226}radium trapped in rock and soil particles to the adjacent interstitial water.

Another common cause of disequilibrium is the aqueous leaching of oxidized uranium from porous formations (usually sandstone) and its subsequent redeposition when reducing conditions are encountered. It is believed that this transport mechanism is the cause of the very rich uranium deposits in the Athabasca sandstone formation of northern Saskatchewan. This same process is known to occur in much of the western North American lignite coal deposits. Because many of these deposits are located near the earth's surface they are often subjected to the leaching and deposition action of surface

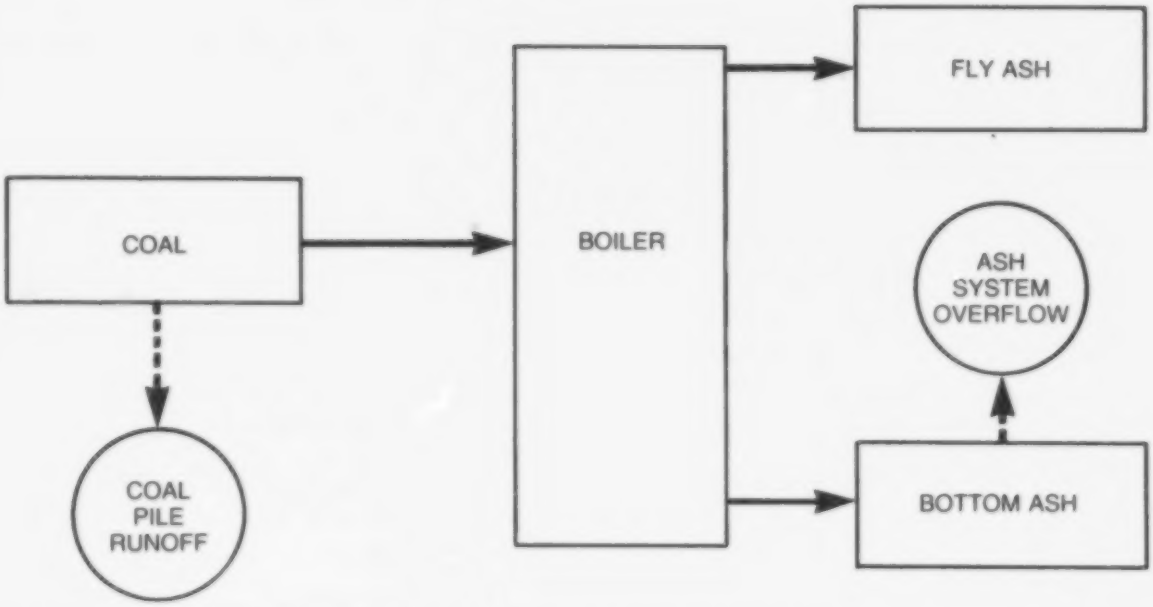


FIGURE 9 PROCESSES WITHIN A GENERATING STATION

TABLE 21 RADIONUCLIDE BALANCE FOR TRENTON GENERATING STATION

Analyte	Coal (µg/g)	Coal Pile Runoff (µg/g)	Bottom* Ash (µg/g)	Fly* Ash (µg/g)	Ash System Overflow (µg/g)
Uranium	1.3	22	4.5	4.8	1.6
Thorium	1.6	102	13.2	13.6	<1
234 Th	2.7×10^{-11}	2.8×10^{-10}	8.0×10^{-11}	8.4×10^{-11}	$<1.2 \times 10^{-9}$
230 Th	8.4×10^{-5}	2.0×10^{-3}	9.8×10^{-11}	8.4×10^{-5}	2.8×10^{-5}
226 Ra	3.3×10^{-7}	5.5×10^{-6}	1.4×10^{-6}	1.2×10^{-6}	$<2.7 \times 10^{-5}$
214 Pb	7.5×10^{-15}	1.7×10^{-13}	4.4×10^{-14}	3.8×10^{-14}	$<2.5 \times 10^{-11}$
214 Bi	5.5×10^{-15}	1.2×10^{-13}	3.0×10^{-14}	2.5×10^{-14}	$<6.0 \times 10^{-14}$
232 Th	5.0	241	12	5.0	<2.5
228 Th	6.6×10^{-10}	3.2×10^{-8}	1.6×10^{-9}	6.6×10^{-10}	$<3.3 \times 10^{-10}$
212 Pb	9.7×10^{-14}	-	8.3×10^{-13}	7.8×10^{-13}	-
208 Tl	7.6×10^{-25}	-	6.7×10^{-24}	6.1×10^{-24}	-
Th/U	1.23	4.64	2.93	2.83	0.31

activities of radionuclides (expressed in Bq) are presented in the appendix

TABLE 22 RADIONUCLIDE BALANCE FOR DALHOUSIE GENERATING STATION

Analyte	Coal (µg/g)	Coal Pile Runoff (µg/g)	Bottom Ash (µg/g)	Fly Ash (µg/g)	Ash System Overflow (µg/g)
Uranium	1.5	11	4.4	10.6	2.5
Thorium	1.6	9	5.3	8.0	2.2
234 Th	2.1×10^{-1}	1.3×10^{-10}	6.2×10^{-11}	9.1×10^{-11}	$<1.2 \times 10^{-9}$
230 Th	5.6×10^{-5}	2.8×10^{-5}	9.7×10^{-5}	9.7×10^{-5}	1.4×10^{-5}
226 Ra	3.3×10^{-7}	$< 2.7 \times 10^{-6}$	1.2×10^{-6}	2.4×10^{-6}	$<2.7 \times 10^{-5}$
214 Pb	7.5×10^{-15}	$< 8.3 \times 10^{-14}$	3.9×10^{-14}	7.6×10^{-14}	$<6.0 \times 10^{-13}$
214 Bi	5.5×10^{-15}	6.1×10^{-14}	2.8×10^{-14}	5.5×10^{-14}	$<6.7 \times 10^{-7}$
232 Th	2.5	5.0	5.0	5.0	<2.5
228 Th	3.3×10^{-10}	6.6×10^{-10}	6.6×10^{-10}	3.3×10^{-10}	$<3.3 \times 10^{-10}$
212 Pb	9.7×10^{-14}	-	3.5×10^{-13}	6.0×10^{-13}	-
208 Tl	7.6×10^{-25}	-	2.6×10^{-24}	4.4×10^{-24}	-
Th/U	1.07	0.82	1.20	0.80	0.88

activities of radionuclides (expressed in Bq) are presented in the appendix

and sub-surface waters When a uranium-containing aquifer contacts a coal seam the sudden change to reducing conditions causes much of the uranium to be deposited in a narrow band at the contact surface of the coal. Although the diffusive removal and transport of ^{222}radon is rapid, as attested by the short half-life of ^{222}radon (3.82 days), the leaching and transport of uranium is a slow process (geological time scale).

Although secular equilibrium has often been assumed for natural radionuclides, evidence suggests that may not universally exist. This is particularly true when geological or environmental processes are at work on the disturbed coal or its resulting ash.

A convenient means of identifying changes in natural radionuclide concentrations as a result of combustion which might in turn effect secular equilibrium is by comparing the relative thorium and uranium concentrations in the coal and combustion residues.

The Th/U ratio is nearly identical for the bottom ash and fly ash for both Trenton G.S. (Table 21) and Lambton G.S. (Table 23); however, the ratio for their

TABLE 23 RADIONUCLIDE BALANCE FOR LAMBTON GENERATING STATION

Analyte	Coal (µg/g)	Coal Pile Runoff (µg/g)	Bottom Ash (µg/g)	Fly Ash (µg/g)	Ash System Overflow (µg/g)
Uranium	0.9	12	5.5	8.8	2.2
Thorium	1.6	29	12.8	19.3	<1
234 Th	1.3×10^{-11}	$< 1.4 \times 10^{-10}$	5.1×10^{-11}	9.1×10^{-11}	$<1.2 \times 10^{-9}$
230 Th	8.4×10^{-5}	5.5×10^{-4}	1.1×10^{-4}	1.3×10^{-4}	1.4×10^{-5}
226 Ra	3.6×10^{-6}	4.9×10^{-6}	1.6×10^{-6}	2.4×10^{-6}	$<2.7 \times 10^{-5}$
214 Pb	6.7×10^{-15}	1.5×10^{-13}	5.3×10^{-14}	8.5×10^{-14}	$<2.5 \times 10^{-13}$
214 Bi	4.8×10^{-15}	1.1×10^{-13}	3.8×10^{-14}	6.2×10^{-14}	$<6.0 \times 10^{-15}$
232 Th	2.5	60	12.4	14	<2.5
228 Th	6.6×10^{-10}	7.6×10^{-9}	1.6×10^{-9}	1.6×10^{-9}	$<3.3 \times 10^{-10}$
212 Pb	9.7×10^{-14}	-	8.5×10^{-13}	1.3×10^{-12}	-
208 Tl	7.6×10^{-25}	-	6.3×10^{-24}	1.1×10^{-23}	-
Th/U	1.78	2.42	2.33	2.20	0.23

activities of radionuclides (expressed in Bq) are presented in the appendix

respective coals differs from the two ashes. For the Dalhousie G.S. (Table 22) and the three western stations (Tables 24 to 26) only minor differences are apparent in the Th/U ratios for the coal, pyrites, bottom ash and fly ash.

There is no known mechanism for the selective separation of U and Th in the combustion process. Both elements produce highly refractory oxides with very little difference in volatility at normal combustion temperatures. It is to be expected, therefore, that the Th/U ratio should remain relatively constant through the combustion process. For all stations, however, the levels of U and Th in the fly ash are higher than in the bottom ash

There are no consistent differences between the activity levels of uranium and its daughters or those of thorium and its daughters in the coal bottom ash and fly ash for all stations Radon will be driven off during combustion but equilibrium should quickly be restored in the ash. The longest radon isotope half-life is only 3.82 days therefore 99 percent of equilibrium will be restored in approximately 30 days There is every

TABLE 24 RADIONUCLIDE BALANCE FOR BOUNDARY DAM GENERATING STATION

Analyte	Coal (μg/g)	Coal Pile Runoff (μg/g)	Bottom Ash (μg/g)	Fly Ash (μg/g)	Ash System Overflow (μg/g)
Uranium	2.0	93	12.7	14.2	5.8
Thorium	3.7	360	22.7	26.8	<1
234 Th	4.2×10^{-11}	1.6×10^{-10}	8.2×10^{-10}	1.3×10^{-11}	$<1.2 \times 10^{-9}$
230 Th	4.2×10^{-5}	4.5×10^{-4}	1.6×10^{-4}	2.0×10^{-4}	1.4×10^{-5}
226 Ra	5.7×10^{-7}	4.4×10^{-6}	3.3×10^{-6}	5.0×10^{-2}	$<2.7 \times 10^{-5}$
214 Pb	1.7×10^{-14}	$< 1.5 \times 10^{-13}$	1.1×10^{-13}	1.6×10^{-13}	$<2.5 \times 10^{-13}$
214 Bi	1.2×10^{-14}	1.0×10^{-13}	7.7×10^{-14}	1.1×10^{-13}	$<6.0 \times 10^{-13}$
232 Th	5.0	774	18	18	<2.5
228 Th	6.6×10^{-10}	9.9×10^{-8}	2.3×10^{-9}	2.6×10^{-9}	3.3×10^{-10}
212 Pb	2.1×10^{-13}	-	1.4×10^{-12}	2.2×10^{-12}	-
208 Tl	1.7×10^{-24}	-	1.1×10^{-23}	1.7×10^{-23}	-
Th/U	1.85	3.87	1.79	1.89	0.09

activities of radionuclides (expressed in Bq) are presented in the appendix

indication that secular equilibrium exists for the naturally occurring radioactive series in the coal down to the respective radium daughters. The combustion process does not appear to alter secular equilibrium at least to this point in the decay series. There is insufficient data, however, to determine whether secular equilibrium exists from the radium daughters through to the stable isotopes at the end of the respective decay series.

4.1 Coal Pile Runoff

As shown in Tables 21 to 26, the first pathway by which radionuclides can enter the environment at coal-fired generating stations is through coal pile runoff or leachate.

When a mineral such as coal is mined and brought to the earth's surface it is subject to the oxidizing and leaching conditions of its new environment. Although all the elements in the radioactive decay series will be affected by this process the more soluble elements will be removed most rapidly. When oxidized to the uranyl ion, uranium is

TABLE 25 RADIONUCLIDE BALANCE FOR SUNDANCE GENERATING STATION

Analyte	Coal (µg/g)	Coal Pile Runoff (µg/g)	Bottom Ash (µg/g)	Fly Ash (µg/g)	Ash System Overflow (µg/g)
Uranium	2.3	46	11.3	12.3	7.9
Thorium	4.0	212	19.4	24.3	13.6
234 Th	3.4×10^{-11}	5.4×10^{-10}	1.2×10^{-10}	1.7×10^{-10}	$<1.2 \times 10^{-9}$
230 Th	9.8×10^{-5}	2.7×10^{-3}	2.5×10^{-4}	1.1×10^{-4}	4.6×10^{-5}
226 Ra	5.2×10^{-7}	1.6×10^{-5}	2.6×10^{-6}	4.1×10^{-6}	$<2.7 \times 10^{-5}$
214 Pb	1.4×10^{-14}	5.2×10^{-13}	9.6×10^{-14}	1.3×10^{-12}	$<2.5 \times 10^{-13}$
214 Bi	1.0×10^{-14}	3.8×10^{-13}	7.3×10^{-14}	9.3×10^{-13}	$<6.0 \times 10^{-13}$
232 Th	5.0	231	24	18	4.47
228 Th	6.6×10^{-10}	3.1×10^{-8}	3.6×10^{-9}	2.6×10^{-9}	2.6×10^{-10}
212 Pb	2.1×10^{-13}	-	1.4×10^{-12}	1.6×10^{-12}	-
208	1.7×10^{-24}	-	1.2×10^{-23}	1.4×10^{-23}	-
Th/U	1.7	4.61	1.72	1.98	1.72

activities of radionuclides (expressed in Bq) are presented in the appendix

generally considered to be the most soluble of the naturally occurring radioactive elements. Radium and lead are of intermediate solubility, whereas thorium and polonium are the least soluble of the group. Thus, oxidative leaching of coal should result in the preferential removal of uranium and possibly some radium and lead. For high sulphur coals, oxidation will also produce sulphuric acid which could accelerate the leaching of uranium, radium and lead. In addition, these acid conditions could result in the dissolution of thorium and polonium.

Thus, the concentrations of radionuclides in the coal pile drainage should be related to the chemical characteristics of the runoff since the conditions which would result in high iron concentrations should also result in high concentrations of uranium, radium and lead. Further, rainfall patterns which are known to cause temporal changes in drainage from the coal piles may also result in varying concentrations or radionuclides in the coal pile runoff.

TABLE 26 RADIONUCLIDE BALANCE FOR MILNER GENERATING STATION

Analyte	Coal (µg/g)	Coal Pile Runoff (µg/g)	Bottom Ash (µg/g)	Fly Ash (µg/g)	Ash System Overflow (µg/g)
Uranium	3.9	54	6.7	8.4	7
Thorium	6.5	192	11.9	13.8	11
234 Th	4.6×10^{-11}	8.2×10^{-10}	1.5×10^{-10}	1.3×10^{-9}	$<1.2 \times 10^{-9}$
230 Th	9.7×10^{-5}	1.8×10^{-3}	9.7×10^{-5}	2.0×10^{-4}	5.6×10^{-5}
226 Ra	9.0×10^{-7}	2.6×10^{-5}	2.3×10^{-6}	3.1×10^{-6}	$<2.7 \times 10^{-5}$
214 Pb	2.5×10^{-14}	5.6×10^{-13}	7.1×10^{-14}	1.1×10^{-14}	$<2.5 \times 10^{-13}$
214 Bi	1.8×10^{-14}	5.0×10^{-13}	5.2×10^{-14}	7.7×10^{-14}	$<6.0 \times 10^{-14}$
232 Th	9.9	146	12	14	7.4
228 Th	1.6×10^{-9}	2.1×10^{-8}	2.0×10^{-9}	2.0×10^{-9}	9.9×10^{-10}
212 Pb	3.3×10^{-13}	-	9.3×10^{-13}	1.3×10^{-12}	-
208 Tl	2.6×10^{-24}	-	7.3×10^{-24}	9.8×10^{-24}	-
Th/U	1.67	3.56	1.78	1.64	1.57

activities of radionuclides (expressed in Bq) are presented in the appendix

Table 27 presents the detailed chemical characteristics of coal pile drainage from the six sites. These wastewaters can be classified into two groups; eastern Canadian with a low pH of about 2.6 and western Canadian with a nearly neutral pH of about 7.7. Comparison with the results of other studies would indicate that these samples are fairly typical in terms of their chemical characteristics.

The gross chemical parameters of the coal pile runoff samples and the results of the radiochemical characterizations of the samples are shown in Table 28. In terms of uranium and thorium, the acidic coal pile drainage samples from the eastern sites contained relatively lower concentrations compare to the nearly neutral conditions at the western sites.

In addition, an examination of the results for the six coal pile runoff samples as presented on Table 28, shows some anomalies in the mass ratio of thorium to uranium. In all cases, except for Dalhousie, the Th/U ratio in the runoff is appreciably higher than in the original coal. The increase in this ratio varies from a low of 1.4 for Lambton (Th/U

TABLE 27 CHEMICAL CHARACTERISTICS OF COAL PILE DRAINAGE

Parameters	Trenton G.S.	Dalhousie G.S.	Lambton G.S.	Boundary Dam G.S.	Sundance G.S.	Milner G.S.
pH (units)	2.65	2.6	2.5	7.5	7.8	7.8
Sp. Conductance (μS)	4800	3300	3400	4300	704	855
Fluoride as F^-	2.9	3.7	0.38	0.7	0.6	0.9
Chloride as Cl^-	418	57.8	37.5	28.1	8.8	11.7
Sulphate as SO_4-	5470	1890	1770	2110	170	193
Suspended Solids	216	430	1690	26600	2960	6870
Total Dissolved Solids	9620	2960	3200	3270	1380	566
Aluminum	261	101	104	1580	433	845
Beryllium	0.043	0.004	0.011	0.031	0.006	0.014
Cadmium	< 0.02	< 0.02	< 0.02	0.03	< 0.02	0.02
Calcium	266	413	291	852	90.5	190
Cobalt	0.8	< 0.1	< 0.1	< 0.1	< 0.1	0.13
Chromium	0.13	< 0.02	0.10	1.23	0.16	0.90
Copper	2.05	0.29	0.29	0.71	0.099	1.39
Iron	1560	289	335	526	101	212
Lead	< 0.2	< 0.2	< 0.2	0.2	< 0.2	0.25
Magnesium	166	25.5	96.5	332	33.1	94.9
Manganese	58.9	58.4	6.24	8.48	0.60	3.05
Molybdenum	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6
Nickel	2.9	0.6	0.3	0.6	0.11	0.43
Phosphorus	7	2	2	15	2	8
Potassium	< 3	3	11	386	32	204
Silver	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Sodium	0.128	217	63	1300	236	162
Strontium	0.129	2.41	2.56	9.93	1.05	3.47
Thorium	< 0.02	< 0.02	< 0.02	< 0.02	0.12	0.13
Titanium	0.22	0.46	3.53	66.3	10.8	39.8
Vandadium	0.22	0.05	0.12	2.16	0.299	1.55
Zinc	15.7	1.2	0.8	1.7	0.31	1.38
Zirconium	< 0.1	1.3	0.1	2.0	0.49	0.95

Note: all analyses reported in mg/L except where otherwise indicated

TABLE 28 CHEMICAL AND RADIOCHEMICAL COMPOSITION OF COAL PILE RUNOFF SAMPLES

Analyte	Trenton G.S.	Dalhousie G.S.	Lambton G.S.	Boundary Dam G.S.	Sundance G.S.	Milner G.S.
pH	2.65	2.6	2.5	7.5	7.8	7.8
Sp. Conductance (µS/cm)	4 800	3 300	3 400	4 300	704	855
Suspended Solids (mg/L)	216	430	1 690	26 600	2 960	6 870
Total Dissolved Solids (mg/L)	9 620	2 960	3 200	3 270	1 380	566
Uranium	22	11	12	93	46	54
Thorium	102	9	29	360	212	192
234 Th	2.8×10^{-10}	1.3×10^{-10}	$<1.4 \times 10^{-10}$	1.6×10^{-10}	5.4×10^{-10}	8.2×10^{-10}
230 Th	2.0×10^{-3}	2.8×10^{-5}	5.5×10^{-4}	4.5×10^{-4}	2.7×10^{-3}	1.8×10^{-3}
226 Ra	5.5×10^{-6}	$<2.7 \times 10^{-6}$	4.9×10^{-6}	4.4×10^{-6}	1.6×10^{-5}	1.5×10^{-3}
214 Pb	1.7×10^{-13}	$<8.3 \times 10^{-14}$	1.5×10^{-13}	$<1.5 \times 10^{-13}$	5.2×10^{-13}	5.6×10^{-13}
214 Bi	1.2×10^{-13}	$<6.1 \times 10^{-14}$	1.1×10^{-13}	1.0×10^{-13}	3.8×10^{-13}	5.0×10^{-13}
232 Th	241	5.0	60	774	231	146
228 Th	3.2×10^{-8}	6.6×10^{-10}	7.6×10^{-9}	9.9×10^{-8}	3.1×10^{-8}	2.1×10^{-8}

Note: all results expressed in µg/L except where noted otherwise
chemical analyses conducted on composite sample
radionuclide concentrations are mean values of multiple samples

coal = 1.78, Th/U runoff = 2.42) to a high of 3.4 for Trenton (Th/U coal = 1.23, Th/U runoff = 4.6) and is not in accordance with what would be predicted from theory. This suggests that either uranium has been previously leached from the suspended coal fines presents in the samples or that during runoff, thorium is being preferentially leached. The first case is certainly possible considering the high solubility of the uranyl ion. In the second case, the preferential leaching of thorium could be due to chemical complexing between thorium and some of the water soluble organic compounds such as carboxylic acids, aldehydes, phenol, or others present in the coal. In addition, it is possible that sufficiently strong reducing conditions exist within the coal pile to prevent formation of the uranyl ion. The chemically complexed thorium appears to be more soluble than uranium under these specific conditions. In most cases the concentrations of ^{238}U, ^{238}Th, ^{226}Ra, ^{214}Pb, and ^{214}Bi are comparable whereas ^{230}Th is elevated for all except Dalhousie. If uranium had been pre-extracted, it should be lower in activity than its other daughters. The preferential extraction of thorium would appear to be the most likely cause when the activity of ^{230}Th is compared to that of uranium and its other daughters.

The temporal variation in uranium and thorium in coal pile runoff from one rainfall event is shown in Figure 10. The unusual behaviour of thorium in this coal pile runoff for which there is no apparent explanation is illustrated in this figure. As occurs with other metals, concentrations of uranium and thorium vary during the rainfall runoff period. This was particularly pronounced for the thorium concentrations. Further study on the behaviour of these two metals in wastewaters of this nature are strongly indicated. From a treatment perspective, flow equalization would be essential to reduce the variations in concentrations of these two metals in order to achieve optimal performance of a treatment process.

These results cannot easily be compared to those found in the literature which are summarized in Table 8. This is due to the relatively high detection limits for the results presented in the literature. The previously reported value, however, would usually fall within the range of the concentrations observed in this study.

The concentrations of uranium ranged between 11 and 93 µg/L, while thorium concentrations ranged between 9 and 360 µg/L. These ranges are greater than those observed in natural surface waters (Uranium 0.1 to 10 µg/L; Thorium 0.01 to 0.1 µg/L) as presented in Section 2 of this report. Although, there is no concensus on the concentrations of uranium and thorium which would be toxic to aquatic life, the concentrations observed exceed those found to be toxic in some specific cases found in the literature. All the uranium concentrations exceed the present desirable drinking

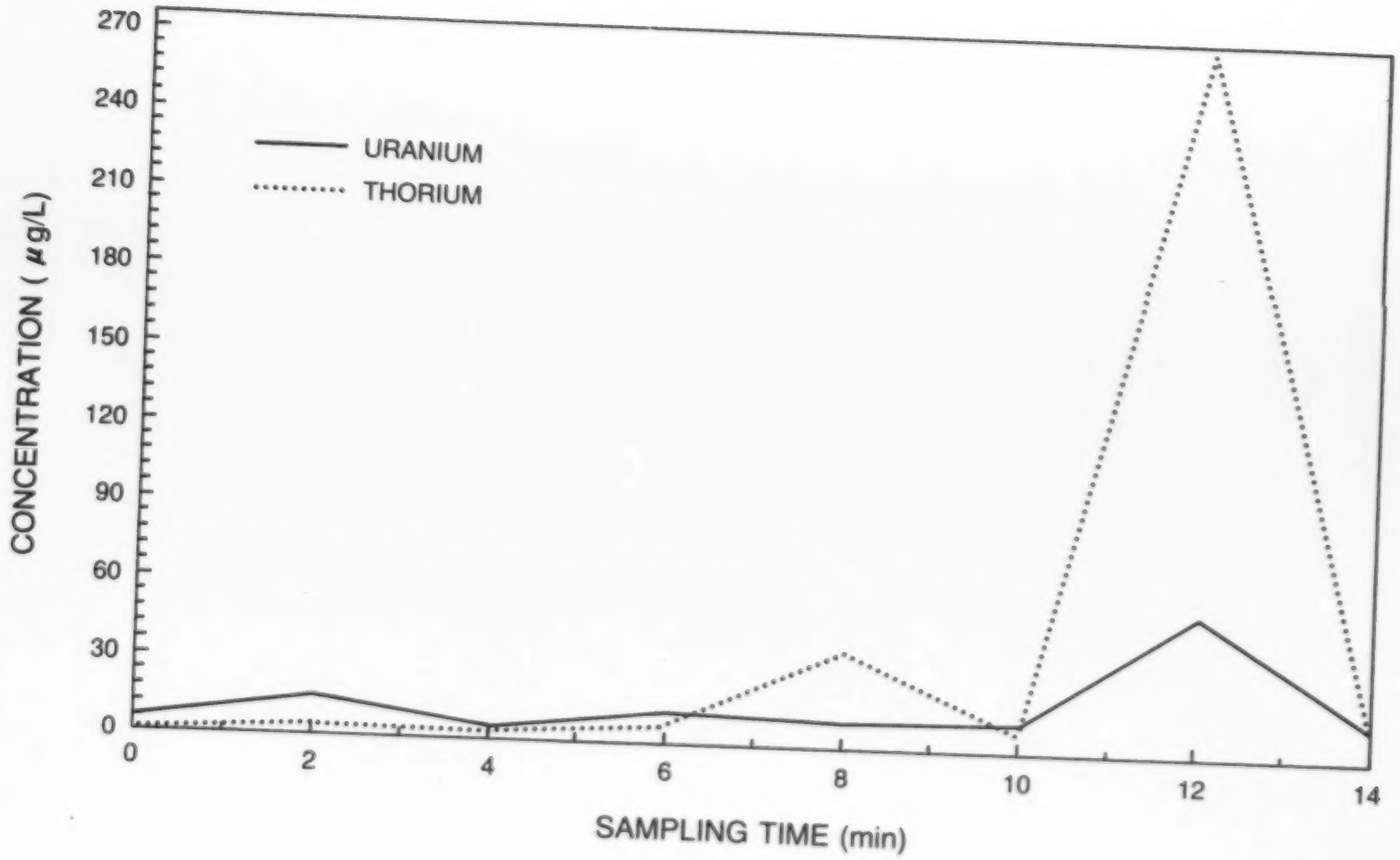


FIGURE 10 TEMPORAL VARIATION IN COAL PILE RUNOFF (Dalhousie Generating Station; June 20, 1982)

water objective (1.0 µg/L as uranyl ion) by at least an order of magnitude and most exceed the maximum acceptable concentration of 20 µg/L (as total uranium). It may be necessary in some instances, therefore, to treat coal pile drainage in order to prevent degradation of the aquatic environment.

4.2 Coal

The second pathway of natural radionuclides into the environment at coal-fired power plants is through emanation of radioactive gaseous elements to the atmosphere or by dusting from the coal pile. This was not investigated during the present study; however, it is possible to examine the relationship between coal rank and radionuclide concentration using data from the analytical program (Table 29).

The bituminous coals could be characterized as having a high sulphur content and an intermediate ash content. Both the sub-bituminous and lignite coals had lower sulphur contents, but the sub-bituminous coal had an ash content twice that of the other two coal ranks. Sulphur content is an important factor since higher values could result in acidic coal pile drainage which could lead to lower uranium and thorium concentrations in the wastewater. The ash content and heat value of the coal is important in the determination of the total radionuclide emissions from a plant. Using a mass balance approach, assuming the same heat content and concentrations of radionuclides in the ash, a station burning coal with a higher ash content would produce a greater absolute amount of radionuclides since a greater amount of ash would be produced per unit of energy.

The uranium and thorium concentrations in the bituminous coal were about half those in the sub-bituminous and lignite coals. When the heat value and ash content of the coal are considered, the greatest relative amounts of uranium and thorium would be produced during the combustion of sub-bituminous, then lignite, then bituminous coal, in decreasing order.

The observed values can be compared to those reported in the literature (Figure 9). Results from the analyses of coal at the six sites investigated were typically in the lower end of the ranges reported in the literature for Canadian coals. In terms of the natural radioactive decay daughters, less than a tenfold difference with respect to coal rank was observed. The exception to this was with ^{226}Ra which was greater in the bituminous coal compared to the two other ranks.

Three coal related solid wastes are produced at generating stations. Pyrites are impurities found in coal which are removed during the coal grinding process. Bottom ash is the combustion residue which remains in the boiler after combustion while fly ash is

TABLE 29 COAL RANK AND RADIONUCLIDE CONCENTRATIONS

Analyte	Bituminous*	Sub-bituminous	Lignite
Ash (%)	10.4	18.5	9.5
Sulphur (%)	3.9	0.3	0.4
Heat Value (MJ/kg)	25.9	22.2	15.7
Uranium	1.2	2.3	2.0
Thorium	1.6	4.0	3.7
234 Th	2.0×10^{-11}	3.4×10^{-11}	4.2×10^{-11}
230 Th	7.5×10^{-5}	9.7×10^{-5}	4.2×10^{-5}
226 Ra	1.4×10^{-6}	5.2×10^{-7}	5.7×10^{-7}
214 Pb	7.2×10^{-15}	1.4×10^{-14}	1.7×10^{-14}
214 Bi	5.3×10^{-15}	1.0×10^{-14}	1.2×10^{-14}
232 Th	3.3	5.0	5.0
228 Th	5.5×10^{-10}	6.6×10^{-10}	6.6×10^{-10}
212 Pb	1.3×10^{-13}	2.1×10^{-13}	2.1×10^{-13}
208 Tl	1.07×10^{-24}	1.7×10^{-24}	1.7×10^{-24}

Note: all results expressed in µg/g unless otherwise indicated
*average of three bituminous coals

removed from stack gases. Frequently these wastes are disposed of at the same site. Table 30 shows the comparative radionuclide concentrations of each of these solid wastes from a generating station burning high sulphur bituminous coal.

The uranium, thorium and decay daughter concentrations were greatest in fly ash followed by the bottom ash and pyrites. The uranium and thorium concentrations in fly ash were about an order of magnitude greater than in the pyrites. The exception to this trend was ^{212}Pb which was about one thousand times greater in the pyrites than in either the fly or bottom ashes.

Thus, it can be concluded that the pyrites, which are uncombustible impurities in the coal, would not represent a significant source of radionuclides in coal-fired generating station wastes.

4.3 Ash System Overflow

Another pathway by which natural radionuclide can enter the environment from coal-fired generating stations is through the overflow from hydraulic ash transport

TABLE 30 RADIONUCLIDE CONCENTRATION IN FLY ASH, BOTTOM ASH AND PYRITES FROM DALHOUSIE GENERATING STATION

Analyte	Fly Ash (µg/g)	Bottom Ash (µg/g)	Pyrites (µg/g)
Uranium	10.6	4.4	0.7
Thorium	8.0	5.3	1.3
234 Th	9.1×10^{-11}	6.2×10^{-11}	1.0×10^{-11}
230 Th	9.7×10^{-5}	9.7×10^{-5}	5.6×10^{-5}
226 Ra	2.4×10^{-6}	1.2×10^{-6}	5.2×10^{-7}
214 Pb	7.6×10^{-14}	3.9×10^{-14}	1.3×10^{-14}
214 Bi	5.5×10^{-14}	2.8×10^{-14}	9.1×10^{-14}
232 Th	5.0	5.0	2.5
228 Th	3.3×10^{-10}	6.6×10^{-10}	3.3×10^{-10}
212 Pb	6.0×10^{-13}	3.5×10^{-13}	1.6×10^{-9}
208 Tl	4.4×10^{-24}	2.6×10^{-24}	9.1×10^{-25}

systems. The chemical characteristics of this wastewater depend on the properties of the ash which is transported, system operation, and rate of blowdown. The chemical characteristics of the ash system overflows are shown in Table 31. With the exception of Trenton G.S. which was acidic, all other stations had overflows which were alkaline.

Table 32 presents the gross chemical characteristics and the radiochemical characterization of the overflows. It should be noted that all analyses were conducted to determine total metal concentrations. These include both dissolved and suspended forms. Although uranium was detected in each sample, thorium was not detected in three of the wastewaters.

In the case of the ash system overflow, the Th/U ratio falls into two distinct categories. In the first, there is no detectable thorium present (Trenton, Lambton and Boundary Dam) although some uranium is present. It may be that the thorium in these situations is not being leached, solubilized or mobilized from the ash. Alternately, the majority of the available uranium may have already departed. In the second case, the Th/U ratio is nearly the same as in the original coal (Dalhousie, Sundance and Milner). In theory, thorium can only occur in aqueous solution if the pH is below 3.5 or if it exists as a soluble complex. Another alternative is that it is present as part of the suspended

TABLE 31 CHEMICAL CHARACTERISTICS OF ASH SYSTEM OVERFLOWS

Parameters	Trenton G.S.	Dalhousie G.S.	Lambton G.S.	Boundary Dam G.S.	Sundance G.S.	Milner G.S.
pH (units)	4.0	7.2	8.4	9.4	8.0	8.7
Sp. Conductance (μS)	2500	1850	7.0	1350	850	740
Fluoride as F^-	0.5	1.6	0.53	1.1	1.4	2.0
Chloride as Cl^-	677	12.9	24.1	12.9	12.3	8.2
Sulphate as SO_4^{-2}	187	891.0	302	256.0	343	319
Suspended Solids	12	191.0	14	0.1	485	390
Total Dissolved Solids	1780	1820.0	603	1040.0	629	565
Aluminum	0.7	16.6	< 0.5	2.2	30.5	22.9
Barium	< 0.05	0.11	< 0.05	0.35	0.64	0.41
Beryllium	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
Cadmium	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Calcium	31.5	406	40.8	64.1	103	120
Cobalt	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Chromium	0.03	0.14	< 0.02	0.10	< 0.02	< 0.02
Copper	0.02	0.04	< 0.01	< 0.01	0.02	0.02
Iron	1.9	22.7	0.2	< 0.1	4.4	4.4
Lead	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Magnesium	49.0	2.89	8.22	17.1	12.1	14.1
Manganese	0.14	0.99	< 0.01	< 0.01	0.06	0.02
Molybdenum	< 0.05	0.11	< 0.05	< 0.05	< 0.05	< 0.05
Nickel	< 0.05	0.07	< 0.05	< 0.05	0.14	< 0.05
Phosphorus	< 0.5	2.2	< 0.5	< 0.5	< 0.5	< 0.5
Potassium	16	14	2	15	7	7
Silver	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Sodium	440	74	119	204	87	37
Strontium	0.31	0.91	0.25	2.56	1.49	1.57
Thorium	< 0.05	< 0.05	< 0.05	< 0.5	< 0.05	< 0.05
Titanium	< 0.05	0.65	< 0.05	< 0.5	0.68	0.98
Vanadium	< 0.05	< 0.05	< 0.05	< 0.5	< 0.05	< 0.05
Zinc	0.11	0.15	< 0.05	< 0.5	0.16	0.08
Zirconium	< 0.05	< 0.05	< 0.05	< 0.5	< 0.05	< 0.05

Note: all analyses reported in mg/L except when otherwise indicated

TABLE 32 CHEMICAL AND RADIOCHEMICAL COMPOSITION OF ASH SYSTEM OVERFLOW SAMPLES

Analyte	Trenton G.S.	Dalhousie G.S.	Lambton G.S.	Boundary Dam G.S.	Sundance G.S.	Milner G.S.
pH	4.0	7.2	8.4	9.4	8.0	8.7
Sp. Conductance (µS/cm)	2 500	1 850	710	1 350	850	740
Suspended Solids (mg/L)	12	191	14	0.1	485	390
Total Dissolved Solids (mg/L)	1 780	1 820	603	1 040	629	565
Uranium	1.6	2.5	2.2	5.8	7.9	7
Thorium	<1	2.2	<1	<1	13.6	11
234 Th	1.2×10^{-9}	$<1.2 \times 10^{-9}$	$<1.2 \times 10^{-9}$	$<1.2 \times 10^{-9}$	$<1.2 \times 10^{-9}$	$<1.2 \times 10^{-9}$
230 Th	2.8×10^{-5}	1.4×10^{-5}	1.4×10^{-5}	1.4×10^{-5}	4.6×10^{-5}	5.6×10^{-5}
226 Ra	$<2.7 \times 10^{-5}$	$<2.7 \times 10^{-5}$	$<2.7 \times 10^{-5}$	$<2.7 \times 10^{5}$	$<2.7 \times 10^{-5}$	$<2.7 \times 10^{-5}$
214 Pb	$<2.5 \times 10^{-11}$	$<6.0 \times 10^{-13}$	$<2.5 \times 10^{-13}$	$<2.5 \times 10^{-13}$	$<2.5 \times 10^{-13}$	$<2.5 \times 10^{-13}$
214 Bi	$<6.0 \times 10^{-14}$	$<6.7 \times 10^{-7}$	$<6.0 \times 10^{-15}$	$<6.0 \times 10^{-13}$	$<6.0 \times 10^{-13}$	$<6.0 \times 10^{-14}$
232 Th	<2.5	<2.5	<2.5	<2.5	4.47	7.4
228 Th	$<3.3 \times 10^{-10}$	$<3.3 \times 10^{-10}$	$<3.3 \times 10^{-10}$	3.3×10^{-10}	2.6×10^{-10}	9.9×10^{-10}

Note: all results expressed in µg/L except where noted otherwise
chemical analyses conducted on composite sample
radionuclide concentrations are mean values of multiple samples

solids. The existence of suspended solids and high concentrations of aluminum and iron is indicated by the Dalhousie, Sundance and Milner ash system overflows (Table 33). Iron and aluminum should only remain in solution if the pH is below 3. In order to determine whether thorium is present in solution or as a suspended solid filtering of the sample prior to analysis would be necessary. The other radionuclides, as measured by alpha or gamma spectroscopy, are at or below the detection limits for this method.

The uranium concentrations in these ash system wastewaters would exceed the desirable drinking water objective of 1 µg/L in all cases but not the maximum acceptable objective of 20 µg/L. Since the uranium and thorium concentrations observed are sufficiently great when compared to the reported work of others described in Section 2, these wastewaters could be toxic to aquatic organisms. This suggests that wastewaters of this type may require treatment prior to their being discharged to the receiving water.

4.4 Concentration Factors

Concentration factors are a convenient means of describing how concentrations of elements can be increased or decreased as a result of some process. Table 33 presents the concentration factors for fly ash and bottom ash in relation to coal.

Uranium and thorium were consistently concentrated in fly ash from the coal between 2.2 and 9.8 times. Concentration factors for the bottom ash in terms of the coal ranged between 1.8 and 12.1 depending on the sampling site. This suggests that radionuclide concentrations in the solid residues from combustion would be between two and ten times greater than in the parent coals. With the exception of thorium at two sites, for the same coal, concentration factors were greater in fly ash than in the bottom ash from the same site. This may be due to some mechanical factors in the furnace design or complex chemical interactions in the coal during combustion in these situations which are not known.

4.5 Comparison of Analytical Techniques

As a means of evaluating the quality of the analytical results it is possible to compare the values obtained by different procedures. A comparison of the uranium and thorium results by NAA with the uranium and thorium daughters as determined by gamma spectroscopy shows reasonable agreement considering the levels present and the fact that the report values represent the average result from 6 discrete samples e.g., for Trenton Generating Station (Table 34). This is true even for coal, with levels approaching the detection limit; coal levels by NAA and gamma spectroscopy were nearly all within one

TABLE 33 CONCENTRATION FACTORS FOR URANIUM AND THORIUM

Generating Station	Element	Fly Ash/ Coal	Bottom Ash/ Coal
Trenton	Uranium	3.7	3.5
	Thorium	8.5	8.3
Dalhousie	Uranium	7.1	2.9
	Thorium	5.0	3.3
Lambton	Uranium	9.8	6.1
	Thorium	8.0	12.1
Boundary Dam	Uranium	7.1	6.4
	Thorium	7.2	6.1
Sundance	Uranium	5.3	4.9
	Thorium	6.1	4.9
Milner	Uranium	2.2	1.7
	Thorium	2.1	1.8

TABLE 34 COMPARISON OF URANIUM RESULTS FROM TRENTON GENERATING STATION AS DETERMINED BY NAA AND GAMMA SPECTROSCOPY

Method	Coal (Bq/g)	Bottom Ash (Bq/g)	Fly Ash (Bq/g)	Coal R/O (Bq/L)	Ash O/F (Bq/L)
Th-234 gamma-spec	0.023	0.069	0.055	0.24	<1
Ra-226 gamma-spec	0.012	0.050	0.045	0.20	<1
Pb-214 gamma-spec	0.009	0.053	0.045	0.19	<0.3
Bi-214 gamma-spec	0.009	0.050	0.042	0.13	<0.1
Th-230 gamma-spec	0.06	0.070	0.060	1.42	0.02
Mean (Th-230 included)	0.022 ± 0.020	0.058 ± 0.009	0.051 ± 0.008	—	~0.02
Mean (Th-230 excluded)	0.014 ± 0.006	0.058 ± 0.009	0.049 ± 0.007	0.21 ± 0.05	----
U-NAA	0.016	0.055	0.059	0.27	0.02

standard deviation of the mean. For all bottom ash and fly ash samples where the levels present are about 5 times background the standard deviation is about ± 15 percent and most results, including ^{230}Th, are within one standard deviation of the mean. For the coal runoff, agreement is good between the NAA result and the gamma results, except for ^{230}Th whose results do not agree. Since the samples analyzed had relatively high thorium concentrations the isotopes appear to have been preferentially concentrated in the runoff.

The comparison between Th by NAA and ^{232}Th and its isotopes by alpha and gamma spectroscopy is very similar to the uranium agreement. Again, considering the levels being measured (at the detection limit to less than 10 times the detection limit) the agreement between the various analytical methods is within acceptable limits.

Some isotopes were not reported consistently, or not at all because their gamma intensities were so weak that for many of the samples the results obtained were at or below the detection limit. Since these isotopes were not critical in establishing equilibrium (except possibly for ^{210}Pb and ^{228}Ac) they were not reported. Both ^{210}Pb and ^{228}Ac are isotopes that would define equilibrium conditions in different parts of their respective decay chains. Unfortunately, these two isotopes could not be detected with sufficient sensitivity to allow them to be consistently measured.

4.6 Summary

The condition of secular equilibrium is an important consideration in understanding the behaviour of natural radionuclides. During the handling and combustion of coals in steam electric generating stations there are many opportunities to disrupt the equilibrium. Based on the radiochemical analyses conducted during this study, there is every indication the secular equilibrium exists for the naturally occurring radionuclide series in coal at least down to the respective radium daughters. The equilibrium in this part of the decay chain appears to be unaffected by the combustion process, however, insufficient data exists to verify the existence of secular equilibrium from the radium daughters to the stable isotopes at the end of the decay chain. Thus secular equilibrium cannot be assumed beyond the respective radium daughters.

In coal pile runoff, concentrations of uranium ranged between 11 and 93 µg/L and thorium concentrations ranged between 9 and 360 µg/L. The radionuclide concentration of this wastewater indicated preferential mobilization of thorium. This appears to be a potentially significant pathway for some radionuclides from coal into the environment. The absolute amount of radionuclides mobilized to the environment would depend on the rank of coal in storage, the volume of wastewater generated by precipitation contacting

the coal pile and the resulting concentration of radionuclides in the coal pile drainage. This combination of factors is very site specific.

Concentrations of uranium exceeded levels where in some cases toxicity to aquatic organisms has been reported. The levels exceeded those normally found in freshwater and the recommended as well as the maximum acceptable drinking water objectives for uranium. Treatment of wastewaters of this type must be considered.

The concentration of radionuclides in coal could be related to the rank and type of coal combustion waste. Fly ash had the highest radionuclide concentration followed by bottom ash and coal pyrites.

The second pathway of radionuclides to the environment at coal-fired generating stations is through overflow from the hydraulic ash system. Concentrations of uranium in this wastewater ranged between 1.6 and 7.9 µg/L and thorium concentrations ranged from less than 1 to 13.6 µg/L. Although these low concentrations do not exceed the maximum acceptable water quality objectives for raw public water supplies of 20 µg/L, they in some cases exceed the desirable objective level for uranium. As with coal pile runoff, in some cases, treatment of this type of wastewater may be necessary.

In terms of total migration of radionuclides to the environment, this pathway is likely more significant than coal pile runoff. Although the radionuclide concentrations are lower in this wastewater compared to coal pile runoff, the volume of overflow is typically hundreds of times greater. Thus the mass discharge of radionuclides would likely be comparatively greater.

A comparison between the uranium and thorium analytical results by neutron activation and the uranium and thorium daughters as determined by gamma spectroscopy showed reasonable agreement.

5 REMOVAL OF RADIONUCLIDES FROM COAL COMBUSTION WASTEWATERS

5.1 Introduction

As mentioned previously, results of the chemical characterizations indicate that concentrations of uranium and thorium in coal pile runoff and ash system overflows can be sufficiently great that some form of treatment may be required to protect the receiving aquatic environment. Also, normally in developing practicable control criteria, consideration of practicable, that is, demonstrated wastewater treatment methods is required. The potential processes for the removal of uranium and thorium from waters are reviewed in this section which begins with a brief review of the aquatic chemistry of these two metals.

Uranium. Uranium is a chemically reactive element that combines directly with most elements in the periodic table (Cotton and Wilkinson, 1962). In aqueous solution, uranium exists in four oxidation states: tri- (U^{+3}), tetra- (U^{+4}), penta- (UO_2^{+}) and hexapositive (UO_2^{+2}) (Grindler, 1962). Uranium ions can produce very complex species because, in addition to the four oxidation states, complex reactions with all ions (except ClO_4^{-}), as well as hydrolytic reactions leading to polymeric ions occur under appropriate conditions (Cotton and Wilkinson, 1962). This ability of uranium to form complex ions in solution is signficant in terms of analytical separation and determination.

Aqueous solutions of uranium have an acid reaction caused by hydrolysis which increases in the order $U^{+3} \rightarrow UO_2^{+2H} \rightarrow U^{+4}$. In natural water, uranium usually occurs as the uranyl ion, UO_2^{+2}, or under reducing conditions, as the uranous ion, U^{+4}. Most uranyl salts are soluble in water, and readily form polymeric species, which can account for the solubility of large amounts of UO_3 in UO_2^{+2} solutions. In water the main species resulting from the hydrolysis of UO_2^{+2} are $(UO_2)_2OH^{+3}$, $(UO_2)_2OH^{+2}$, and $(UO_2)_3(OH)_4^{+2}$ (Cotton and Wilkinson, 1962; McNeely et al., 1979).

The uranous ion, is soluble only in acidic water, although it can exist in considerable concentrations; mono as well as polynuclear species are formed:

$$U^{+4} + H_2O = U(OH)^{+3} + H^{+}$$

The U^{+4} ion gives insoluble precipitates with fluorides, phosphates and iodates from acid solutions (Cotton and Wilkinson, 1962).

Thorium. Thorium exists in solution as a relatively small, highly charged cation which undergoes extensive hydrolysis. The species formed are complexed and depend on the condition of pH, nature of anions and concentration. Since thorium has only one oxidation state (+4), oxidation - reduction reactions do not need to be considered which greatly simplifies its aqueous chemistry (Hyde, 1960).

Most salts of thorium are insoluble in water except for the nitrates, sulphates, chlorides and perchlorates (De Ment and Dake, 1946). In perchlorate solutions below pH 3, the main ion appears to be TH^{+4} (aq), whereas, polymeric species such as $Th(TH(OH)_3)_n^{n+4}$ (n=1,2,3...) are formed at a higher pH or in highly concentrated solutions. In solution with anions other than perchlorate, thorium forms complexed species which may additionally be partially hydrolyzed and polymeric (Cotton and Wilkinson, 1962).

5.2 Treatability of Coal Combustion Wastewaters

Few studies have investigated the removal of radionuclides from coal pile and ash disposal site drainages. The limited number of analyses performed on these wastewaters indicate very low concentrations of uranium and thorium. The concentrations in coal leachates (U: 2×10^{-3} to 130×10^{-3} mg/L and Th: 1×10^{-3} to 90×10^{-3} mg/L) were found to be lower than in ash leachates (U: 0.02×10^{-3} to 0.11×10^{-3} mg/L and Th: 0.05×10^{-3} to 0.17×10^{-3} mg/L).

Although radioactivity cannot be chemically destroyed, it is possible to concentrate and separate it so that the bulk of the effluent can be discharged. The potential treatability process for radioactive effluent include biological and physical-chemical methods.

5.2.1 Conventional Treatment. The behaviour of uranium and thorium in conventional wastewater treatment consisting of pH adjustment, coagulation, flocculation and sedimentation has not been well documented. In fact, removal methods appear to have been developed as concentration processes for industrial purposes rather than for the removal of uranium and thorium from industrial wastewaters in large-scale pollution control plants. Consequently, no demonstrated and therefore practicable wastewater treatment for coal pile runoff and ash system overflows from large coal-fired stream electric generating stations can be said to exist at this time. The following are only some of the possibilities for wastewater treatment development.

Based on the chemistry of these metals, inference can be made on their possible removal using conventional technologies.

Thorium, which is insoluble in the neutral pH range would likely precipitate as a metal hydroxide during conventional physical-chemical treatment. Removal would, therefore, be related to the efficiency of the suspended solids removal system (sedimentation basin or clarifier). Thorium, could, in some wastewaters become complexed and not follow the pH versus solubility relationship. For example, thorium is known to form soluble complexes with polyphosphates and oxalic acid. In these forms, the concentrations of thorium would not be reduced during treatment.

The removal of uranium using conventional treatment would likely be much more difficult due to the metal's four valence states, the solubility of uranyl salts in waters with a high redox potential and the solubility of uranous ion in reducing environments. The solubility of uranium tetracarbonate would likely preclude its removal from carbonate-rich wastewaters.

It may be possible to employ conventional treatment under acidic conditions with the addition of phosphates or fluorides which form insoluble precipitates with uranium. This would likely have to be used as a second stage of treatment with a first stage used to remove all other metals with one soluble at low pH. It would also be necessary to adjust the effluent pH following uranium removal to the neutral range.

5.2.2 Biological Methods. Aquatic micro-organisms have the ability to concentrate metals from solution (Collins, 1960). This phenomenon may be made of use for the biological treatment of wastewaters containing uranium. Gloyna and Ewing (1957) found that the activated sludge process was able to remove 60 to 90 percent of uranium in the range of 0.098 to 2000 mg/L. The lower limit is comparable to uranium concentrations in coal combustion wastewaters. Their study, however, was aimed at recovering uranium from saline solutions.

In another study, batch experiments were conducted to examine the removal of uranium from nuclear fuel processing wastewater by sorption and/or complexation of the metal by *Pseudomonas aeruginosa*, a bacteria (Schumate et al., 1978). The initial uranium concentration range of 10 to 100 mg/L was reduced by 90 percent and approached equilibrium after a contact time of only 10 minutes. These results may not be directly applicable to the present study since even the lowest uranium concentration investigated was an order of magnitude greater than those in coal and ash leachates. Nevertheless, the results may provide some useful insight as to the identification of factors that influenced the rate of uranium uptake, such as, temperature, pH and initial uranium concentration.

5.2.3 Physical - Chemical Methods.

Chemical Precipitation. Small quantities of uranium can be separated from waste solutions by precipitation with hydrogen peroxide (H_2O_2). This procedure, normally carried out in a strongly acidic medium (optimum pH: 2.0 to 2.5) yields $UO_4 \times H_2O$; thorium, zirconium and vanadium also precipitate (Grindler, 1962; Gens, 1966).

An organic precipitant, 8-Hydroxyquinaldine (oxine) precipitates hexavalent uranium, (UO_2^{+2}) from weakly acidic or basic solutions. A large number of other elements, including thorium, are also precipitated by oxine. Aldehyde ammonia and 2-aminopyridine effectively precipitate UO_3 (Grindler, 1962).

The removal of radium from uranium mine tailings slurries is commonly accomplished by the addition of $BaCl_2$ to the decanted solution. This results in the co-precipitation of radium and barium sulphate as a sludge. Subsequent to the addition of $BaCl_2$, the treated water is retained in a pond area where the co-precipitate gradually settles (Barton and Comrie, 1980).

Trace amounts of thorium can be co-precipitated quantitatively with a wide variety of insoluble hydroxides, including lanthanum, ferric and zirconium hydroxide (Hyde, 1960). Thorium in higher concentrations (20 mg/L) has been effectively precipitated by the addition of soaps. With a potassium palmitate (handsoap) concentration of 200 percent of the stoichiometric amount of thorium, and a concentration of impurity ions of 20 000 mg/L, decontamination factors of more than 20 were reached in one step (Drathen and Erichsen, 1977).

Adsorption and Aeration. Radon gas in well waters of Maine containing radium concentrations up to 0.15 Bq/L was effectively removed by adsorption onto granular activated carbon. In a continuous flow process, the activated carbon continued to remove the radon beyond the expected point of column saturation, and steady-state removal occurred. It was speculated that this is due to the radioactive decay of radon adsorbed on the column. Diffused aeration, was also found to be effective, as well as economical, for the removal of radon from this water (Hess et al., 1981)

In another study (Moore, 1975) well water containing unusually high concentrations of radium-226 (4.1 Bq/L) was treated by adsorption onto acrylic fibres impregnated with oxides of manganese. Two columns filled with these fibres were operated in series at flow rates of about 8 L/min. After 2650 L of water had been processed, the effluent still had less than 10 percent of the ^{226}Ra concentration of water entering the system.

Solvent Extraction. Solvent extraction methods have been successfully used for the separation of uranium. A common method of solvent extraction of uranyl nitrate, formed by the dissolution of metallic uranium in nitric acid, employs di-ethyl ether as a solvent. The conditions which affect the extraction of uranium from aqueous solution by organic solvent are: the composition of the aqueous phase, the temperature, and the time of equilibration (Grindler, 1962).

Solvent extraction has also been employed for the separation of thorium. The extraction of thorium onto organic solvents can be performed following the complex formation between thorium and x-thenoyltrifluoroacetone (TTA). A pH of 1 is optimal for this extraction procedure. The extraction of thorium onto organic solvents, mainly hydrochloric acid systems, has also been successfully utilized (Hyde, 1960).

Ion Exchange. Fluidize-bed ion exchange has been used to remove uranium oxide (U_3O_8) from each liquor. U_3O_8 concentrations were reduced from about 1000 mg/L to less than 1 mg/L. The flow rate was 45 L/min, and resin loadings of about 75 000 g/L were achieved. A pilot scale fluidized bed ion exchange system that was operated at Elliot Lake, Ontario also produced satisfactory results (Anon., 1982).

Electrolytic Membrane Separation. In order to remove radionuclides selectively Innova Inc. recently developed an electrolytic membrane separation (EMS) system. In this procedure, unlike ion exchange, only the radioactive ions are removed leaving the non-radioactive ions behind. The removal of cations is achieved by reversing the direction of ion migration, such that, the ions move from the anolyte compartment through which the solution flows to the catholyte which contains the cathode (Dietrichsen, 1982).

Summary. Results of chemical characterizations indicate that concentrations of uranium and thorium in coal-fired steam electric power station wastewater can be sufficiently great that some form of treatment may be required to protect the receiving aquatic environment. As a part of the development of discharge criteria, consideration of practicable and thus demonstrated treatment methods is required. Several methods have been proposed for the removal of uranium and thorium; however, these have tended to represent advanced technologies and they have not as yet been practicably demonstrated in this application.

The chemistry of these two metals would suggest that physical/chemical treatment technology could possibly be considered. This would likely include pH adjustment coagulation, flocculation and sedimentation. Similarly, this approach has not been demonstrated in a full-scale treatment plant. A deficiency exists, therefore, in the

treatability of uranium and thorium in the complex wastewaters of coal-fired generating stations.

CONCLUSIONS AND RECOMMENDATIONS

Based on the review of the technical literature, results of the analytical program and analysis of these data, the following conclusions and recommendations were made.

- At the present time there are seemingly conflicting reports on the chemical toxicity of uranium and thorium. There are insufficient data to accurately assess the environmental effects of the chemical toxicity of naturally occurring uranium and thorium on aquatic systems. The information available, however, indicates that released uranium and thorium will ultimately reside in sediments, organic debris or aquatic organisms. Sediments have been neglected, on the whole, as a depot of both uranium and thorium in aquatic ecosystems. The literature indicates that a variety of freshwater and marine organisms have accumulated uranium and thorium and several toxic concentrations have been suggested.
- The chemical toxicity of uranium and thorium is thought to be the principal concern rather than its radioactive properties. This line of thinking has been followed by many researchers. The chemical toxicity of uranium would likely affect aquatic populations before its associated levels of radioactivity would show any detrimental affects.
- In terms of bioaccumulation and bioconcentration, little can be safely concluded about the threat or hazard of uranium and thorium to aquatic organisms. Bioaccumulation has been demonstrated in several instances but the amounts vary from case to case. Once uranium and thorium are released to the aquatic environment there is the potential for them to become biologically available and the possibility for accumulation exists.
- Although thorium is more abundant naturally than uranium, it appears to be less bioavailable in the natural water column due to its stronger bonding properties. Local environmental conditions and physiological factors appear to strongly influence the toxicity of uranium and thorium. In general, the limited data and different test procedures reported to date make the comparison of tests and results difficult and the evaluation of this data tentative.
- Measurements of radionuclides in coal-fired power plant effluents indicate the potential for bioaccumulation in food chains. The few studies of radionuclide uptake by biota in the vicinity of power plants, however, do not provide a sufficient basis

from which to predict the magnitude of the problem. Further comparative studies of the movement and uptake of radionuclides in critical terrestrial and aquatic food chains near coal-fired plants in different geographical areas, utilizing different types of coal, under different climatic, soil and water quality conditions, are still required.

- In the literature, radionuclide concentrations in both U.S. and Canadian coals were indicated to vary over a wide range. A set of averages for U.S. coals of ^{238}U: 1.7 mg/kg, ^{232}Th: 4.5 mg/kg and ^{40}K: 0.20 mg/kg were lower than the corresponding concentrations of these radionuclides in "typical" soil. The radionuclide content both of U.S. and Canadian coals appears to vary with rank; uranium had a higher upper concentration and spanned a wider range of values for lignite and bituminous coals compared to sub-bituminous coals. Comprehensive analytical data on radionuclides in Canadian coals were lacking; the uranium and thorium decay products in particular had not been thoroughly quantified.
- Analysis of coal samples from six sites in Canada indicated that measurable concentrations of uranium and thorium were present in all samples. Sub-bituminous coals had the greatest concentrations followed by lignite and bituminous coals. This is in agreement with previously reported results which suggested that western coals (sub-bituminous and lignite) have higher radioactivity compared with eastern coals (bituminous).
- Analyses of solid residues from one site indicated that the highest uranium and thorium concentrations were present in the fly ash followed by the bottom ash and pyrites. In all cases, the uranium and thorium concentrations in the fly ash were always greater than the bottom ash from the same site.
- The concentration factors for uranium and thorium in coal to fly ash for the six sites ranged between 2.1 and 9.8. The concentration factors for coal to bottom ash ranged from 1.8 to 12.1.
- During the handling and combustion of coal in steam electric generating stations there are many opportunities to disrupt secular equilibrium in the coal and ashes. Based on the radiochemical analyses conducted during this study, there is every indication that secular equilibrium exists for the naturally occurring radionuclide series in coal down to the respective radium daughters. The equilibrium in this part of the decay chain appears to be unaffected by the combustion process, however, insufficient data exist to verify the existence of secular equilibrium from the

radium daughters to the stable isotopes at the end of the decay chain. Thus secular equilibrium cannot be assumed beyond the respective radium daughters.

- Coal pile runoff appears to be a potentially significant pathway for some radionuclides from coal into the aquatic environment. In this wastewater, concentrations of uranium ranged between 11 and 93 µg/L and thorium concentrations ranged between 9 and 360 µg/L. The greatest concentrations were found in runoff from lignite coal. Compared to those of uranium elevated thorium concentrations did not correspond to predictions based on simple chemical theory. This suggested that some complexing of thorium had occurred.

  The absolute amount of radionuclides mobilized to the environment would depend on the rank of the coal in storage, the volume of the wastewater generated by precipitation contacting the coal pile and the resulting concentration of radionuclides in the coal pile drainage. This combination of factors is very site specific and their interactions are not well understood.

  Some concentrations of uranium exceeded levels where toxicity to aquatic organisms has been reported. The concentrations exceeded those normally found in freshwater and the recommended water quality objectives for uranium. Treatment of wastewaters of this type must be considered.

- The second pathway of radionuclides to the environment at coal-fired generating stations is through overflow from the hydraulic ash system. Concentrations of uranium in this wastewater ranged between 1.6 and 7.9 µg/L and thorium concentrations ranged between less than 1 and 13.6 µg/L. A strong relationship between iron and aluminum and thorium were observed in the ash system overflows. Thorium concentrations greater than those of uranium were observed, which indicates that some complexing of thorium had occurred; however, without total and soluble thorium analyses, definite conclusions cannot be made.

  Although the concentrations of uranium in ash contacted waters did not exceed the objective for raw public water supplies of 20 µg/L, in some cases the desirable objective level of 1 µg/L uranium were exceeded. As with coal pile runoff, treatment of this type of wastewater may be necessary in some cases. In terms of absolute migration of radionuclides to the environment, this pathway is likely more significant than coal pile runoff. Although the radionuclide concentrations are lower than those of coal pile drainage, the volume of the overflow is typically hundreds of times greater. The mass discharge of radionuclides, therefore, would likely be comparatively greater.

- Concentrations of uranium and thorium in the coal pile runoff and ash systems overflows were at least an order of magnitude lower than those believed to cause short-term or acute toxicity. As measurable concentrations were quantified, it is possible for bioaccumulation or chronic toxicities to occur.
- Likewise, the radioactivities in the wastewater samples due to uranium, thorium and their decay daughters are well below those activities known to cause short-term or acute biological effects. It is possible that long-term or genetic effects could occur from exposure of aquatic species to the low-level radioactivity of such wastewaters.
- In some cases, coal related wastewaters may require treatment prior to their discharge in order to prevent damage to the receiving aquatic environment. Several technologies have been suggested for the removal of uranium, thorium and specific decay daughters, however, these have tended to be industrial processes for their concentration and recovery rather than for use in large-scale wastewater treatment plants. Insufficient data exists to allow conclusions to be made whether or not conventional physical - chemical treatment technology could be used to remove uranium and thorium from complex wastewaters of this nature. Consequently, no demonstrated or practicable wastewater treatment methods for coal pile runoff or ash system overflow exists at this time. It would appear that the only means to reduce the total emissions or uranium and thorium in ash system wastewaters at this time is to reduce the volume of this overflow.
- Based on direct experience during this study, it can be concluded that reliable analytical methods are currently available to quantify extremely low concentrations of many radionuclides in coal, fly ash, bottom ash, and ash system overflow samples. The quantification of many radionuclides in coal pile runoff samples, particularly in the presence of iron, however, is still extremely difficult. In the case of samples of coal pile runoff analyzed during this study, it was necessary to develop a special protocol for sample preparation. Analytical techniques must be refined to allow for greater precision and accuracy since this pathway is the greatest potential source of radionuclides entering the surrounding aquatic environment.

Based on this study, the following recommendations were made:

- In view of the general lack of reliable data on the effects of low-level, long-term exposure of aquatic and terrestrial wildlife species to radioactivity, it is recommended that research be supported which would define radiation levels which could be considered harmful. Based on the specific activities of decay daughters of the

natural radionuclides, acceptable concentrations of decay daughters in effluent streams should be determined.

- Pilot-scale treatability studies should be conducted to demonstrate that uranium and thorium can be removed from complex wastewaters using conventional treatment technologies. Testing of this nature could be used to define optimum treatment methods specific to coal and ash contaminated wastewaters.
- At this time, there is a lack of quantitative data on the leachability of uranium and thorium from either bottom or fly ash from Canadian coals. It is recommended that suitable leaching tests be conducted on representative ash samples in order to determine their potential for leaching over short- and long-term periods.

REFERENCES

Adams, J.A.S., J.K. Osmond, and J.J.W. Rogers, "The Geochemistry of Thorium and Uranium", in: Physics and Chemistry of the Earth, L.H. Ahrens, F. Press, K. Rankama, and S.K. Runcorn (eds.) Pergamon Press, New York (1959).

Anderson, J.B., E.C. Tsivoglou and S.D. Shearer, "Effects of Uranium Mill Wastes on Biological Fauna of the Animas River (Colorado - New Mexico)", in: Radioecology, V. Schultz, A.W. Klements (eds.), (Proc. Symp. Colorado 1961), Reinhold, New York, pp. 373-383 (1963).

Anon., International Atomic Energy Agency, "Effects of Ionizing Radiation on Aquatic Organisms and Ecosystems", IAEA Tech. Report No. 172 (1976).

Anon., "Ion Exchange: New Design Offers Continuous Process", Environmental Science and Technology, 10(10):977 (October, 1976).

Anon., "Methods for Chemical Analysis of Water and Wastes", Environmental Monitoring and Support Laboratory, Environmental Research Centre, Cincinnati, OH, EPA 625/6-79-033a (1976).

Anon., International Commission on Radiological Protection, Radiation Protection, ICRP No. 26, Pergamon Press, Oxford (1977).

Anon., "Radiochemical Procedures for Determination of Selected Members of the Uranium and Thorium Series", Canmet Report 78-22 (January, 1979).

Anon., United States Committee on Health and Environmental Effects of Increased Coal Utilization, Report on Health and Environmental Effects of Increased Coal Utilization, Environmental Health Perspectives, 36:135-154 (1980).

Anon., "Guidelines for Surface Water Quality, Volume 1, Inorganic Chemical Substances, Uranium", Inland Waters Directorate, Water Quality Branch, Environment Canada, Ottawa, Canada (1983).

Bagg, D.L., Comparison of Radiological Impacts of Lakeview Thermal and Pickering Nuclear Generating Station Atmospheric Releases Using Different CDM Model Data Bases", Atmospheric Environment Service Report ARQB-81-020-N, Downsview, Ontario (March, 1981).

Barclay, R., "Biological Effects of Ionizing Radiation", Saskatchewan Research Council (1981).

Barton, A. and D.C. Comrie, "Treating Mine Wastes - Maintaining the Sensitive Environmental Balance in Remote Regions", Water and Pollution Control (May, 1980).

Bates, D.V., Murray, J.W. and V. Raudsepp, "Royal Commission of Inquiry into Uranium Mining", Commissioner's Report, Volume I, Province of British Columbia (October, 1980).

Baturin, G.N., "Uranium Content in Caspian Sea Sediments", At. Energ. (USSR) 21:516-517 (1966).

Baturin, G.N., A.V. Kochenov, and K.M. Shimkus, "Uranium and Minor Metals in Columns of Bottom Sediments of the Black and Mediterranean Seas", Geokhimiya 1:41-50 (1967).

Bayda, E.D., "The Cluff Lake Board of Inquiry Final Report", Government of Saskatchewan (1978).

Bayliss, R.J. and H.M. Whaite, "A Study of the Radium Alpha-activity of Coal Ash and Particulate Emission at a Sydney Power Station", Air and Wat. Pollut. Int. J. 10:813-819 (1966).

Beck, H.L., C.V. Gogolak, K.M. Miller and W.M. Lowder, "Perturbations on the Natural Radiation Environment Due to the Utilization of Coal as an Energy Source", in: Natural Radiation Environment III, Volume 2, Proceed. of Symposium at Houston, Texas, April 23-28, 1978, T.F. Gesell and W.M. Lowder (ed.) (1978).

Beck, H.L., C.V. Gogolak, K.M. Miller and M.W. Lowder, "Perturbations on the Natural Radiation Environment Due to the Utilization of Coal as an Energy Source", Proceedings of the Symposium on the Natural Radiation Environment - III, CONF - 780422, U.S. Dept. of Energy (1979).

Beck, H.L. and K.M. Miller, "Some Radiological Aspects of Coal Combustion", IEEE Transactions on Nuclear Science, NS-27, (1):689 (Feb., 1980).

Bhat, S.G. and S. Krishnaswamy, "Isotopes of Uranium and Radium in Indian Rivers", Proc. Indian Acad. Sci. Sect. A 1:1-17 (1969).

Blaylock, B.G., "Chromosomal Polymorphism in Irradiated Natural Populations of Chironomus", Genetics 53:131-136 (1966).

Blaylock, B.G. and J.R. Trabalka, "Evaluating the Effects of Ionizing Radiation on Aquatic Organisms", Adv. Rad. Bio. 7:103-152 (1978).

Bloch, S., "Some Factors Controlling the Concentration of Uranium in the World Ocean", Geochemica et Cosmochimica Acta 44:373-377 (1980).

Breger, I.A., M. Deul and R. Meyrowitz, "Geochemistry of Mineralogy of a Uraniferous Subbituminous Coal", Economic Geology, 50(6):610 (1955).

Bringmann, G. and R. Kuhn, "The Toxic Effects of Wastewater on Aquatic Bacteria, Algae and Small Crustaceans", Gesundheits-Ing. 80:115 (1959).

Bringmann, G. and R. Kuhn, "Water Toxicology Studies with Protozoans as Test Organisms", Gesundheits-Ing. 80:239 (1959).

British Columbia Hydro and Power Authority, "Hat Creek Project-Radiological Impact Evaluation", EIS Ref. No. 7 (May, 1981).

Bryan, G.W., A. Preston and W.L. Templeton, "Accumulation of Radionuclides by Aquatic Organisms of Economic Importance in the United Kingdom", in: Disposal of Radioactive Wastes into Seas, Oceans and Surface Waters, CONF-660507, IAEA, Vienna, pp. 623-627 (1966).

Cameron, A.R. and T.F. Birmingham, "Radioactivity in Western Canadian Coals Geological Survey of Canada" (June, 1970).

Chapman, W.H., H.L. Fisher and M.W. Pratt, "Concentration Factors of Chemical Elements in Edible Aquatic Organisms", UCRL - 50564 (1968).

Cherry, D.S., R.K. Guthrie, J.H. Rodgers Jr., J. Cairns, Jr., and K.L. Dickson, "Responses of Mosquitofish (*Gambusia affinis*) to Ash Effluent and Thermal Stress", Trans. Amer. Fish. Soc. 105:686-694 (1976).

Choppin, G.R. and J.W. Morse, "An Integrated Study of the Behaviour of Transuranic Elements in the Marine Environment", A progress report to the U.S. Department of Energy, NTIS (1981).

Coles, D.G., R.C. Ragaini and J.M. Ondov, "Behaviour of Natural Radionuclides in Western Coal-Fired Power Plants", Environmental Science and Technology, 12(4):442 (1978).

Collins, J.C., Radioactive Wastes, Their Treatment and Disposal, John Wiley and Sons Inc., New York (1960).

Cotton, F.A. and G. Wilkinson, Advanced Inorganic Chemistry, A Comprehensive Text, Interscience Publishers, John Wiley and Sons Inc., New York (1962).

Curtis, K.E., "Trace Element Content of Western Canadian Coals", Ontario Hydro Research Division, File No. 837.214 (July, 1980).

Cushman, R.M., S.G. Hildebrand, R.H. Strand and R.M. Anderson, "The Toxicity of 35 Trace Elements in Coal to Freshwater Biota: A Data Base with Automated Retrieval Capabilities", NTIS Report No. ORNL/TM-5793, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1977).

Davis, E.C. and W.J. Boegly, Jr., "Coal Pile Leachate Quality", J. Envir. Engin. Div. 107:399-417 (1981).

Dearborn Environmental Consulting Services, "Identification and Characterization of Contaminants Potentially Present in Canadian Coal Wastewaters and Assessment of the Impacts of These Contaminants on the Aquatic Environment", DSS File No. 51SS.KE145-1-0640 (March, 1982a).

Dearborn Environmental Consulting Services, "Characterization and Treatability of Drainage from Coal Piles at Canadian Steam Electric Stations", Economic and Technical Review Report EPS 3-WP-82-4, Water Pollution Control Directorate, Environment Canada (August, 1982b).

DeJong, L.E.D.D., "Tolerance of *Chlorella vulgaris* for Metallic and Non-metallic Ions", Anton. V. Leeuwenhoek 31:301-313 (1965).

Delany, A.C. and R.L. Fleischer, "Increase in Uranium Concentration in Streams Draining Rocky Flats, Colorado", J. of Geochemical Exploration 9:53-62 (1978).

De Ment, J. and H.C. Dake, Rarer Metals, Chemical Publishing Company, Inc., New York (1946).

Dietrichsen, B., Laboratory Director, Innova Inc., Clearwater, Florida, personal correspondence (August, 1982).

Donaldson, L.R. and K. Bonham, "Effects of Chronic Exposure of Chinook Salmon Eggs and Alevins to Gamma Irradiation", Trans. Am. Fish. Soc. 99:112-119 (1970).

Doudoroff, P. and M. Katz, "Critical Review of Literature on the Toxicity of Industrial Wastes and Their Components to Fish, II. The Metals, as Salts", Sewage and Industrial Wastes 25:802 (1953).

Drathen, V.H. and L.V. Erichsen, "Technische Seifen - eine Moeglichkeit zum Dekontamination thoriumhaltiger Abwasser", Atomkernenergie (ATKE), BD. 29, Germany (1977).

Dunn, C., The Biogeochemical Expression of Deeply Buried Uranium Mineralization in Saskatchewan, Canada", J. Geochem. Explor. 15:437-452 (1981).

Dvorak, A.J. and B.G. Lewis, "Impacts of Coal-fired Power Plants on Fish, Wildlife and Their Habitats", U.S. Fish and Wildlife Service FWS/OBS-78/29 (1978).

Dyck, W., "Geochemical Studies in the Surficial Environment of the Beaverlodge Area, Saskatchewan", Geological Survey of Canada, paper 74-32 (1974).

Eisenbud, M. and H.G. Petrow, Radioactivity in the Atmospheric Effluents of Power Plants that Use Fossil Fuels, Science, (144):288 (1964).

Eisenbud, M., Environmental Radioactivity, Academic Press, New York (1973).

Essington, E.H., E.B. Fowler, R.O. Gilbert and L.L. Eberhardt, "Plutonium, Americium and Uranium Concentrations in Nevada Test Site Soil Profiles", in: Transuranium Nuclides in the Environment, Symposium Proceedings, San Francisco, 1975, STI/PUB/410, International Atomic Energy Agency, Vienna, Austria (1976).

Farmer, B.M., C.E. Styron, C.A. Phillips, B. Robinson and W.H. Westendorf, "The Assessment of the Radiological Impact of Western Coal Utilization, Phase I", Monsanto Research Corp., Mound Laboratory Report, Miamisburg, OH (Jan., 1977).

Foster, R.F. and D. McCannon, "Relationship Between the Concentration of Radionuclides in Columbia River", in: Biological Problems in Water Pollution, C.M. Tarzwell (ed.), USPHS 999-WP-25, R.A. Taft Sanitary Engineering Centre, Cincinnati, OH, Technical Report W60-3, XV (1962).

Franson, M.A. (man. ed.), "Standard Methods for the Examination of Water and Wastewater", fifteenth edition, American Public Health Association, Washington, D.C. (1980).

Fukai, R., "Some Biogeochemical Considerations on the Radioactive Contamination of Marine Biota and Environments", First International Congress on Radiation Protection, Rome, Italy, 1966, pp. 391-394 (1966).

Furr, A.K., T.F. Parkinson, W.D. Youngs, C.O. Berg, W.H. Gutenmann, I.S. Pakkala and D.J. Lisk, "Elemental Content of Aquatic Organisms Inhabiting a Pond Contaminated with Coal Fly Ash", New York Fish and Game Journal 26(2):154-161 (1979).

Garner, R.J., "Transfer of Radioactive Materials from the Terrestrial Environment to Animals and Man", Critical Reviews in Environmental Control No. 2, pp. 337-385 (1972).

Garner, R.J., "Transfer of Radioactive Materials from the Terrestrial Environment to Animals and Man", CRC Press, Chemical Rubber Co., Cleveland, OH (1972).

Gens, T.A., U.S. Patent 3,238,014 (1966).

Gloyna, E.F. and B.B. Ewing, "Uranium Recovery from Saline Solutions by Biological Slimes", Nucleonics, 15(1):78 (January, 1957).

Gluskoter, H.G., R.R. Ruch, W.G. Miller, R.A. Cahill, G.B. Drehir and J.K. Kuhn, "Trace Elements in Coal: Occurrence and Distribution", Illinois State Geological Survey Circular 499, Urbana, IL. (1977).

Goldberg, E.D. and M. Koide, "Geochronological Studies of Deep-sea Sediments by the Ionium/Thorium Method", Geochim. Cosmochim. Acta 26:417 (1962).

Greening, F.R., "Radionuclides in Fly Ash", Ontario Hydro Research Division, File No. 837.71 (March, 1981).

Grindler, J.E., "The Radiochemistry of Uranium, Argonne National Laboratory, Argonne, Illinois", National Academy of Sciences and National Research Council Report NAS-NS-3050 (March, 1962).

Gross, F. and F.F. Koczy, "Photometric Measurements of the Growth of Phytoplankton Cultures", Medd. Oceanogr. Inst. No. 10 (1946).

Gus'kova, V.N., Gurfein, L.N. and A.I. Tikhonova, "Uranium Action in a Reservoir", Gidrobiol. Zh. 2:53-57 (in Russian) (1966).

Guthrie, J.E., "Radioecology of Insects in Aquatic Environments", The Manitoba Entomologist 4:33-45 (1970).

Hamilton, E.I., "The Concentration of Uranium in Man and His Diet", Health Physics 22:149-153 (1972).

Hansen, R.O. and P.R. Stout, "Isotopic Distributions of Uranium and Thorium in Soils", Soil Science 105:44 (1968).

Hanson, W.C., "Ecological Considerations of Depleted Uranium Munitions", USAEC Report, La-5559, Los Alamos Scientific Laboratory, NTIS (1974).

Hanson, W.C., "Ecological Considerations of Natural and Depleted Uranium", in: Natural Radiation Environment III. Volume 2, Proceed. of Symposium at Houston, Texas, April 23-28, 1978, T.F. Gesell and W.M. Lowder (eds.) (1978).

Havlik, B., "Radium in Aquatic Food Chains: Radium Uptake by Freshwater Algae", Radiation Research 46:490-505 (1971).

Health and Welfare Canada, Environmental Radioactivity in Canada, Radiological Monitoring Semi-Annual Report, 80-EHD-51 (Jan.-June, 1979).

Heslop, R.B., Inorganic Chemistry - A Guide to Advanced Study, Elsevier Publishing Co., New York (1963).

Hess, C.T., S.A. Norton, W.F. Brutsaert, J.E. Lowny and C.F. Weiffenbach, "Investigation of ^{222}Rn, ^{226}Ra and U in Air and Groundwaters of Maine", Land and Water Resources Center, University of Maine at Orono, Project B-017-Me (June, 1981).

Hill, C.R., "Polonium-210 in Man", Nature 208:423-428 (1965).

Hoffman, J., "Experimental Determination of Uranium in Living Freshwater Algae", Water Pollution Abs. 15 (April, 1942).

Holm, E. and B. Persson, "Radiochemical and Radioecological Studies of Natural and Artificial Alpha-emitting Radionuclides", in: Natural Radiation Environment III, Volume 2, Proceed. of Symposium at Houston, Texas, April 23-28, 1978, T.F. Gesell and W.M. Lowder (eds.) (1978).

Holtzman, R.B., "^{226}Ra and the Natural Airborne Nuclides ^{210}Pb and ^{210}Po in Arctic Biota", in: Radiation Protection, Synder, W. (ed.), Pergamon Press, New York, pp. 1087-1096 (1968).

Holtzman, R.B., "Concentrations of the Naturally Occurring Radionuclides Ra-226, Ph-210 and Po-210 in Aquatic Fauna", in: Proc. of 2nd National Symp. on Radioecology, Nelson, D.J. and F.C. Evans (eds.), USAEC Oak Ridge, pp. 535-546 (1969).

Hyde, E.K., "The Radiochemistry of Thorium", Lawrence Radiation Laboratory, University of California, Berkley, California, National Academy of Sciences and National Research Council Report NAS-NS 3004 (January, 1960).

Jinks, S.M. and M. Eisenbud, "Concentration Factors in the Aquatic Environment", Radiat. Data Rep. 13:243-247 (1972).

Justyn, J., "Uptake of Natural Radioisotopes by Aquatic Organisms", Hydrobiol. Studies, 3:145-171 (1976).

Justyn, J. and S. Lusk, "Evaluation of Natural Radionuclide Contamination of Fishes in Streams Affected by Uranium Ore Mining and Milling, Zoologicke listy 25(3):265-274 (1976).

Kauranen, P. and J.K. Miettinen, "Polonium and Radiolead in Some Aqueous Ecosystems in Finland", Helsinki Univ. Dept. of Radiochem. Annual Report, NYO-3446-14 Paper 27 (1970).

Kawabata, T., "Studies on the Sorption and Release of Radionuclides by River Sediments", J. of Radiation Research 8(1):20-31 (1967).

Kharkar, D.P., J. Thomson, K.K. Turekian and W.D. Forster, "Uranium and Thorium Decay Series Nuclides in Plankton from the Caribbean", Limnol. Oceanog. 21:294-299 (1976).

Koczy, F.F., "The Natural Radioactive Series in Organic Material", in: Radioecology, V. Schultz and A.W. Klement, Jr. (eds.), Reinhold Publishing Corporation, New York (1963).

Koenuma, A., "The Effect of Uranyl Nitrate on Fertilization in *Urechis unicinctus* and *Hemicentrotus pulcherrimus*", Dobutsugaku Zasshi, 65:281-286, Chemical Abstracts, Vol. 51:15016 (1956).

Koren, K. and A. Bull, "Determination of Radioiodine in Milk", Health Physics, 5:225-226 (1961).

Kovalsky, V.V., I.E. Vorotnitskaya and V.S. Lekarev, "Biogeochemical Food Chains in Uranium in Aquatic and Terraneous Organisms", in: Radioecological Concentration Processes, Proceedings of an International Symposium, Stockholm, April 25-29, 1966, B. Aberg and F.P. Hungate (eds.) (1966).

Kreiger, H. and B. Jacobs, "Analysis of Radioactive Contaminants in By-Products from Coal-Fired Power Plant Operations", Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency Report, EPA-600/4-78-039.

Lee, H., T.O. Peyton, R.V. Steele and R.K. White, "Potential Radioactive Pollutants Resulting from Expanded Energy Programs", prepared for U.S. Dept. of Commerce, NTIS PB-272519 (August, 1977).

Lopatkina, A.P., V.S. Komarov, A.N. Sergeyev and A.C. Andreyev, "Brief Communications on Concentration of Uranium by Living and Dead Peat-Forming Plants", Eng. Trans. Geochem. Int. USSR. 7:277-282 (1970).

Lucas, H.F., D.N. Edgington and P.J. Colby, "Concentrations of Trace Elements in Great Lakes Fishes", J. Fish. Res. Bd. Canada 27:677-684 (1970).

Lush, D. and S.M. Swanson, "Pathway Analyses and Transfer Coefficients", presented at Seminar on Comparative Ecotoxicity of Uranium Mining and Milling Emissions, Saskatoon, Sask., Saskatchewan Research Council (1981).

MacCormack, J., "Trace Elements in Saskatchewan Coal-Fired Power Plants", Environmental Protection Service, Regina (August, 1979).

Mackenzie, A.B., M.S. Baxter, I.G. McKinley, D.S. Swan and W. Jack, "The Determination of ^{134}Cs, ^{137}Cs, ^{210}Pb, ^{226}Ra, and ^{228}Ra Concentrations in Nearshore Marine Sediments and Seawater", J. Radioanal. Chem. 48:29-47 (1979).

Martin, J.E., E.D. Harward and D.T. Oakley, "Comparison of Radioactivity from Fossil Fuel and Nuclear Power Plants", U.S. Dept. of Health, Education and Welfare (Nov., 1969).

McBride, J.P., R.E. Moore, J.P. Witherspoon and R.E. Blanco, "Radiological Impact of Airborne Effluents of Coal and Nuclear Plants", Science, (202):1045 (1978).

McKee, J.E. and H.W. Wolf, Water Quality Criteria, second edition, California State Water Resources Control Board, Publication No. 3-A (1963).

McNeely, R.N., V.P. Neimanis and L. Dwyer, "Water Quality Sourcebook, A Guide to Water Quality Parameters", Inland Waters Directorate, Water Quality Branch, Ottawa (1979).

Milligan, J.D. and R.J. Ruane, "Effects of Coal-ash Leachate on Groundwater Quality", U.S. Environmental Protection Agency, EPA-600/7-80-066 (1980).

Moffett, D. and M. Tellier, "Uptake of Radioisotopes by Vegetation Growing on Uranium Tailings", Can. J. Soil Sci. 57:417-424 (1977).

Moore, W.S., "Amazon and Mississippi River Concentrations of Uranium, Thorium and Radium Isotopes", Earth Planet. Sci. Lett. 2:231-234 (1967).

Moore, W.S., "Radium Removal from Drinking Water", Nature, 253:262 (January, 1975).

Moore, J.W. and D.J. Sutherland, "Distribution of Heavy Metals and Radionuclides in Sediments, Water and Fish in an Area of Great Bear Lake Contaminated with Mine Wastes", Arch. Environ. Contam. Toxicol. 10:329-338 (1981).

Morgan, G.E., "The Absorption of Radioisotopes by Certain Microorganisms", Quarterly Journ. of the Florida Academy of Sciences, 24:94 (1961).

Morris, J.S. and G. Bobrowski, "The Determination of ^{226}Ra, ^{214}Pb and ^{214}Bi in Fly Ash Samples from Eighteen (18) Coal-Fired Power Plants in the United States", in: Proceedings, Fifth International Ash Utilization Symposium, Spencer, J. and C. Whieldon (eds.), U.S. Dept. of Energy, METC/SP-79/10, pp. 460-469 (1979).

Morrison, W.G., "Energy, Environment and Power Generation in Canada", Ontario Hydro, Toronto (1978).

Muller, E.F. and D.L. Bagg, "Radioactive Atmospheric Emissions of a Large Coal-Fired and a CANDU Generating Station of Comparable Size", presented at the 20th Annual International Conference of the Canadian Nuclear Association, Montreal (June, 1980).

Murray, R.L., Understanding Radioactive Waste, Batelle Pacific Northwest Laboratory, Batelle Press, Columbus, OH (1982).

Nakahara, N., T. Koyanagi and M. Saiki, "Temperature Effect on the Concentration of Radionuclides by Marine Organisms", J. Radiat. Res. 18:122-131 (1977).

Nakamura, R., Y. Suzuki and T. Ueda, "Influences of Marine Sediment on the Accumulation of Radionuclides by Green Algae (*Ulva pertusa*)", J. Radiat. Res. 16:224-236 (1975).

Nelson, D.J. and B.G. Blaylock, "The Preliminary Investigation of Salivary Gland Chromosomes of *Chironomus tentans* Fabr. from the Clinch River", in: Radioecology, V. Schultz and A.W. Klement, Jr. (eds.), Reinhold, New York, pp. 367-372 (1963).

Newmarch, C.B., "Geology of the Crowsnest Coal Basin, with Special Reference to the Fernie Area", B.C. Dept. of Mines, Bulletin No. 33 (1953).

Nikolaev, D.C. et al., "The Concentration of Uranium in the Waters of the Black Sea", Dokl. Akad. Nauk USSR 132:1411-1412 (in Russian) (1960).

Odum, E.P., Fundamentals of Ecology, W.B. Saunders Co., Philadelphia (1971).

O'Kelley, J.C., "The Potential Effects of Depleted Uranium on Range C-24 Upon the Algal Flora of Rocky Creek on Elgin Air Force Base", Florida, NTIS Report afatl-TR-76-98 (1976).

Ondov, J.M., R.C. Ragaini and A.H. Biermann, "Characterization of Trace Element Emissions from Coal-Fired Power Plants, presented at the Third International Conference of Nuclear Methods in Environmental and Energy Research, University of Missouri, CONF-771072-6 (Feb., 1978).

Ophel, I.L., "Radiation Effects in Contaminated Aquatic Ecosystems and Their Relation to Laboratory Studies", in: Methodology for Assessing Impacts of Radioactivity on Aquatic Ecosystems, IAEA Series No. 190, Vienna, pp. 211-216 (1979).

Panel on the Trace Element Geochemistry of Coal Resource Development Related to Environmental Quality and Health, U.S. Dept. of Energy Report DOE/CH/93015-3 (1980).

Panson, A.J. and R.G. Charles, "Carbonate Chemistry of Uranium", in: Energy and Mineral Resource Recovery, ANS Topical Meeting CONF-770440, p. 728 (1977).

Patzer, R.G., "Concentration Factors and Transport Models for Radionuclides in Aquatic Environments, a Literature Report", U.S. Environmental Protection Agency, EPA-600/3-76-054 (1976).

Pentreath, R.J., "Radionuclides in Marine Fish", Oceanography and Marine Biology, An Annual Review 15:365-460 (1977).

Polikarpov, G.G., G. Zaitsev, G.V. Barinov and C. Porchevsky, "General Features of the Concentration of Processes of Radioactive Substances by Hydrobins in Different Seas of the World Ocean", in: Radioecological Concentration Process-Proceedings of an International Symposium, B. Aberg and F.P. Hungate (eds.), Oxford, Pergamon Press (April, 1966).

Poston, T.M., "Observations on the Bioaccumulation Potential of Thorium and Uranium in Rainbow Trout (*Salmo gairdneri*)", Bull. Environ. Contam. Toxicol. 28:6820690 (1982).

PRCMA, "Poplar River Cooperative Monitoring Arrangement, 1981", Fourth Quarter Data Exchange (1981).

Pshenin, L.P., "The Accumulation of U-UX, by Nitrogen-Fixing Microorganisms of the Black Sea", Water Pollution Abs. 34(10):1946 (1962).

Purdom, C.E. and D.S. Woodhead, "Radiation Damage in Fish", in: Genetics and Mutagenesis in Fish, J.H. Schroeder (ed.), Springer-Verlag, Berlin, pp. 67-73 (1973).

Risik, N.S., in: Artificial and Natural Radionuclides in Marine Life, edited by G.G. Polikarpov, translated by Israel Program for Scientific Translations (1975), 40-67 (1973).

Rodman, M.R., L.I. Gordon and A.C-T. Chen, "Extraction of Uranium from Seawater: Evaluation of Uranium Resources and Plant Siting", prepared for the U.S. Department of Energy, Grand Junction, Colorado, Volume I (1979).

Rothschild, H.C., "A Criteria Digest on Radioactivity in the Environment", National Research Council of Canada Rep. No. NRCC 13566 (1973).

Sackett, W.M. and G. Cook, "Uranium Geochemistry of the Gulf of Mexico", Trans. Gulf Coast Assoc. Geol. Soc. 19:233-238 (1969).

Sackett, W.M., T. Mo, R.S. Spalding and M.E. Exner, "A Re-evaluation of the Marine Geochemistry of Uranium", in: Radioactive Contamination of the Marine Environment, STI/PUB/313, International Atomic Energy Agency, Vienna, Austria (1973).

Sakaguchi, T., T. Horikoshi and A. Nakajima, "Uptake of Uranium from Sea Water by Microalgae", J. Ferment. Technol. 56(6):561-565 (1978).

Sheppard, M.I., "The Environmental Behaviour of Uranium and Thorium", Atomic Energy of Canada Ltd., Whiteshell Nuclear Research Establishment, Pinawa, Manitoba (1980).

Sheppard, M.I., "The Environmental Behaviour of Uranium and Thorium", Atomic Energy of Canada Ltd., Report 6795 (1980).

Sheppard, M.I., "The Environmental Behaviour of Radium", Atomic Energy of Canada Ltd., Report 6796 (1980).

Shumate II, S.E., G.W. Strandberg and J.R. Parrott, Jr., "Biological Removal of Metal Ions from Aqueous Process Streams", presented at the Symposium of Biotechnology in Energy Production and Conservation, Gattinburg, Tennessee (May, 1978).

Sill, C.W. and R.L. Williams, "Preparation of Actinides for Alpha-Spectrometry without Electrodeposition", Anal. Chem. 53:412 (1981).

Smithson, G.L., Statement: "Radiochemical Measurement of Radionuclides in the Uranium and Thorium Series", in: Province of British Columbia Royal Commission of Inquiry into Uranium Mining, Phase 6, 54 p. (October 30, 1980).

Smithson, Dr. G., personal communication, Head, Analytical Laboratory, Saskatchewan Research Council (January, 1982).

Styron, C.E., "Preliminary Assessment of the Impact of Radionuclides in Western Coal on Health and Environment Monsanto Research Corporation", Mound Laboratory Report MLM-2497, Miamisburg, OH (1978).

Styron, C.E. and B. Robinson, "A Preliminary Radiological Impact Assessment of Western Coal Utilization", Proceedings of the 4th Joint Commission on Sensing of Environmental Pollutants, New Orleans (Nov., 1977).

Styron, C.E., C.T. Bishop, V.R. Casella, P.H. Jenkins and W.H. Yanko, "Assessment of the Impact of Radionuclides in Coal Ash", presented at the International Symposium on Health Impacts of Different Sources of Energy, Nashville, TN (June, 1981a).

Styron, C.E., C.T. Bishop, V.R. Casella, P.H. Jenkins and W.H. Yanko, "Assessment of the Radiological Impact of Coal Utilization, II", Radionuclides in Western Coal Ash, Monsanto Research Corp., Mound Laboratory Report MLM-2810, Miamisburg, OH (1981b).

Styron, C.E., C.T. Bishop, V.R. Casella, P.H. Jenkins and W.H. Yanko, "Assessment of the Impact of Radionuclides in Coal Ash", presented at International Symposium on Health Impacts of Different Sources of Energy, IAEA-SM-254, Vienna (1981).

Sullivan, M.F., "Absorption of Actinide Elements from the Gastrointestinal Tract of Rats, Guinea Pigs and Dogs", Health Physics 38:159 (1980).

Swanson, S.M., "Increased Radionuclide Levels in Fish Near a Saskatchewan Uranium Mine and Mill", Saskatchewan Research Council C-805-44-A-81 (1981).

Swanson, S.M., "Levels and Effects of Radionuclides in Aquatic Fauna of the Beaverlodge Area, Sask.", SRC C-806-5-E-82 (1982).

Swanson, V.E., J.H. Medlin, J.R. Hatch, J.L. Coleman, G.H. Wood, S.D. Woodruff and R.T. Hiltebrand, "Collection, Analysis, and Evaluation of Coal Samples in 1975", Open File Report 76-468, U.S. Geological Survey, Washington, D.C. (1976).

Tannenbaum, A. and H. Silverstone, "Factors Affecting Uranium Poisoning", in: Toxicology of Uranium, A. Tannenbaum (ed.), McGraw-Hill Book Co., New York (1951).

Tarzwell, C.M. and C. Henderson, "The Toxicity of Some of the Less Common Metals to Fishes", Trans. Seminar on Sanitary Engineering Aspects of the Atomic Energy Industry, Robt. A. Taft, San. Engrg. Centr. TID-7517 (1956).

Tarzwell, C.M., "The Use of Bio-Assays in Relation to the Disposal of Toxic Wastes", Third Ontario Industrial Waste Conference, Pollution Control Board of Ontario, 117 (1956).

Tarzwell, C.M., "Water Quality Criteria for Aquatic Life. Biological Problems in Water Pollution", RATSEC, Public Health Service, 246 (1957).

Tarzwell, C.M., "Disposal of Toxic Wastes", Ind. Wastes 3:2,48 (1958).

Templeton, W.L., "Effects of Radiation on Aquatic Populations", in: Environmental Toxicity of Aquatic Radionuclides: Models and Mechanisms, M.W. Miller and J.N. Stannard, (eds.), Ann Arbor Science Publ. Inc., Ann Arbor, pp. 287-297 (1976).

Till, J.E., S.V. Kaye and J.R. Trabalka, "The Toxicity of Uranium and Plutonium to the Developing Embryos of Fish", NTIS Report No. ORNL - 5160, UC-41 Health and Safety, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1976).

Thompson, S.E., C.A. Burton, D.J. Quinn and Y.C. Ng, "Concentration Factors of Chemical Elements in Edible Aquatic Organisms UCRL - 50564, Rev. 1, Lawrence Livermore Laboratory Biomedical Division (1972).

Tracy, B.L. and F.A. Prantl, "Radiological Implications of Thermal Power Production", presented at International Symposium on Health Impacts of Difference Sources of Energy, IAEA-SM-254, Vienna (1981).

Tracy, B.L. and F.A. Prantl, "Radiological Implications of Thermal Power Production", presented at the International Symposium on Health Impacts of Different Sources of Energy, Nashville, Tennessee (June, 1981).

UNSCEAR, "Sources and Effects of Ionizing Radiation", United Nations Scientific Committee on the Effects of Atomic Radiation 1977 Report, United Nations, New York (1977).

Uthe, J.V. and E.G. Bligh, "Preliminary Survey of Heavy Metal Contamination of Canadian Freshwater Fish", J. Fish. Research Bd. of Canada 28(5):786-789 (1971).

Vanderploeg, H.A., D.C. Parzyck, W.H. Wilcox, J.R. Kercher and S.V. Kaye, "Bioaccumulation Factors for Radionuclides in Freshwater Biota", Oak Ridge National Laboratory ORNL-5002 (1975).

Van Hook, R.I., "Potential Health and Environmental Effects of Trace Elements and Radionuclides from Increased Coal Utilization", NTIS Report No. ORNL-5367, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1978).

Wagner, P., D.R. Dreesen, E.M. Wewerka and N.R. Greiner, "Radioactive Emissions from Coal Production and Utilization", U.S. Dept. of Energy, Progress Report No. LA-8618-PR (July 1978 - Sept. 1979).

Wangen, L.E. and M.D. Williams, "Elemental Deposition Downwind of a Coal-Fired Power Plant", Water, Air and Soil Pollution 10:33-44 (1978).

Weast, R.C. and M.J. Astle, "CRC Handbook of Chemistry and Physics", CRC Press, Inc., West Palm Beach, Florida (1978).

Whitehead, N.E. and R.R. Brooks, "Aquatic Bryophytes as Indicators of Uranium Mineralization", The Bryologist 72(4):501-507 (1971).

Zimmerman, J.B. and V.S. Armstrong, "The Determination of Radium-226 in Uranium Ores and Mill Products by Alpha Energy Spectrometry", Canmet Report 76-11 (December, 1975).

APPENDIX

NOTE: Results in parentheses have been calculated.

For cases where results are expressed as less than the detection limit, one half the detection limit has been used in the calculation of the mean and standard deviation.

TABLE A1 TRENTON GENERATING STATION

Analyte	Method	Coal		Bottom Ash		Fly Ash		Coal Pile R/O		Ash System O/F	
		(µg/g)	(Bq/g)	(µg/g)	(Bq/g)	(µg/g)	(Bq/g)	(µg/L)	(Bq/g)	(µg/L)	(Bq/L)
U	NAA	1.3±0.4	(1.6x10-2 ±0.49x10-2)	4.5±0.9	(5.5x10-2 ±1.1x10-2)	4.8±1.2	(5.9x10-2 ±1.5x10-2)	22±21	(27x10-2 ±26x10-2)	1.6±1.6	(2.0x10-2 ±2.0x10-2)
Th	NAA	1.6±0.7	(6.4x10-3 ±2.8x10-3)	13.2±2.1	(53.2x10-3 ±8.4x10-3)	13.6±2.8	(54.8x10-3 ±11.2x10-3)	102±110	(411x10-3 ±444x10-3)	<1	(4x10-3)
U Series											
^{234}Th	γ	(2.68x10-11 ±0.82x10-11)	0.023±0.007	(8.07x10-11 ±3.98x10-11)	0.069±0.034	(6.81x10-11 ±1.63x10-11)	0.055±0.014	(2.8x10-10 ±3.2x10-10)	0.24±0.28	(<1.2x10-9)	<1
^{230}Th	α	(8.4x10-5 ±1.4x10-5)	0.06±0.01	(9.8x10-5 15.6x10-5)	0.07±0.04	(8.4x10-5 ±5.6x10-5)	0.06±0.04	(2.0x10-3 ±0.2x10-4)	1.42±0.3	(2.8x10-5 ±1.4x10-5)	0.02±0.01
^{226}Ra	γ	(3.28x10-7 ±1.09x10-7)	0.012±0.004	(13.6x10-7 ±2.19x10-7)	0.050±0.008	(12.3x10-7 ±1.37x10-7)	0.045±0.005	(5.5x10^{6} ±4.4x10-6)	0.20±0.18	(<2.7x10-6)	<0.1
^{214}Pb	γ	(7.30x10-15 ±0.83x10-15)	0.009±0.001	(44.2x10-15 ±5.83x10-15)	0.053±0.007	(37.5x10-15 ±3.33x10-15)	0.045±0.004	(1.7x10-13 ±1.5x10-13)	0.20±0.18	(<2.5x10-13)	<0.3
^{214}Bi	γ	(5.46x10-15 ±0.61x10-15)	0.009±0.001	(30.3x10-15 ±3.64x10-15)	0.05±0.006	(25.4x10-15 ±1.82x10-15)	0.042±0.003	(1.2x10-13 ±1.1x10-13)	0.20±0.18	(<6.0x10-14)	<0.1
^{210}Pb	γ	-	-	-	-	-	-	-	-	(<7x10-7)	<2
Th Series											
^{232}Th	α	(5.0±2.5)	0.02±0.01	(12±9.9)	0.05±0.04	(5.0±5.0)	0.02±0.02	(201±37)	0.97±0.15	(<2.5)	<0.01
^{228}Th	α	(6.6x10-10)	0.02	(16x10-10 ±13x10-10)	0.05±0.04	(6.6x10-10 ±6.6x10-10)	0.02±0.02	(3.3x10-8 ±0.3x10-9)	0.98±0.13	(<3.3x10-10)	<0.01
^{212}Pb	γ	(9.68x10-14 ±3.88x10-14)	0.005±0.002	(83.3x10-14 ±11.6x10-14)	0.043±0.006	(77.5x1-.-14 ±5.81x10-14)	0.040±0.003	-	-	-	-
^{212}Bi	γ	-	-	-	-	-	-	-	-	(<2.7x10-13)	<0.15
^{208}Tl	γ	(7.62x10-25 ±3.04x10-25)	0.005±0.002	(67.0x10-25 ±10.6x10-25)	0.044±0.007	(61.0x10-25 ±4.57x10-25)	0.040±0.003	-	-	-	-

TABLE A2 DALHOUSIE GENERATING STATION

Analyte	Method	Coal (µg/g)	Coal (Bq/g)	Pyrite (µg/g)	Pyrite (Bq/g)	Bottom Ash (µg/g)	Bottom Ash (Bq/g)	Fly Ash (µg/g)	Fly Ash (Bq/g)	Coal Pile R/O (µg/g)	Coal Pile R/O (Bq/g)	Ash System O/P (µg/g)	Ash System O/P (Bq/L)
U	NAA	1.5±0.7	(1.8x10-2 ±8.6x10-2)	0.7±0.1	(0.8x10-2 ±0.2x10-2)	4.4±1.6	(5.4x10-2 ±1.7x10-2)	10.6±4.3	(13.0x10-2 ±5.2x10-2)	11±3	(14x10-2 ±4x10-2)	2.5±1.0	(3.0x10-2 ±1.2x10-2)
Th	NAA	1.6±0.5	(6.4x10-3 ±2.0x10-3)	1.3±0.5	(5.2x10-3 ±2.0x10-3)	5.3±1.7	(21x10-3 ±6.8x10-3)	8.0±1.9	(3.2x10-3 ±7.6x10-3)	9±11	(36x10-3 ±44x10-3)	2.2±1.6	(8.8x10-3 ±5.6x10-3)
U Series													
^{234}Th	γ	(2.1x10-11 ±1.40x10-11)	0.018±0.012	(1.04x10-11 ±1.04x10-11)	0.009±0.009	(6.18x10-11 ±4.67x10-11)	0.053±0.040	(9.09x10-11 ±4.78x10-11)	0.078±0.041	(1.3x10-10 ±2.3x10-11)	0.11±0.02	(<1.2x10-9)	<1
^{230}Th	α	(5.6x10-5 ±2.79x10-5)	0.04±0.02	(5.6x10-5 ±2.8x10-5)	0.04±0.02	(9.7x10-5 ±5.6x10-5)	0.07±0.04	(9.7x10-5 ±7.0x10-5)	0.07±0.05	(2.8x10-5)	0.02	(1.4±10-5 0.56x10-5)	0.01±0.004
^{226}Ra	γ	(3.28x10-7 ±1.09x10-7)	0.012±0.004	(5.19x10-7 ±0.546x10-7)	0.019±0.002	(12.0x10-7 ±3.01x10-7)	0.044±0.011	(23.8x10-7 ±1.37x10-7)	0.087±0.005	(<2.7x10-6	<0.10	(<270x10-7)	<1
^{214}Pb	γ	(7.50x10-15 ±2.50x10-15)	0.009±0.003	(12.5x10-15 ±0.16x10-15)	0.015±0.005	(39.2x10-15 ±10.8x10-15)	0.047±0.0013	(75.8x10-15 ±6.66x10-15)	0.091±0.008	(<8.3x10-14)	<0.10	(<2.5x10-13)	<0.3
^{214}Bi	γ	(5.45x10-15 ±1.82x10-15)	0.009±0.003	(9.09x10-15 ±3.03x10-15)	0.015±0.005	(28.4x10-15 ±6.66x10-15)	0.047±0.011	(55.2x10-15 ±1.82x10-15)	0.091±0.003	(<6.1x10-14	<0.10	(<60x10-15)	<0.1
^{210}Pb	γ	-	-	-	-	-	-	-	-	-	-	(<6.67x10-7)	<2
Th Series													
^{232}Th	α	(2.5±0.99)	0.01±0.004	(2.5±0.99)	0.01±0.004	(5.0±5.0)	0.02±0.02	(5.0±5.0)	0.02±0.02	(5.0)	0.02	(<2.5)	<0.01
^{228}Th	α	(3.3x10-10 ±1.32x10-10)	0.01±0.004	(3.3x10-10 ±1.32x10-10)	0.01±0.004	(6.6x10-10 ±3.3x10-10)	0.02±0.01	(3.3x10-10 ±3.3x10-10)	0.01±0.01	(6.6x10-10)	0.02	(<3.3x10-10)	<0.01
^{212}Pb	γ	(9.68x10-14 ±1.94x10-14)	0.005±0.001	(15.5x10-14 ±3.88x10-14)	0.008±0.002	(36.8x10-14 ±5.81x10-14)	0.018±0.003	(60.0x10-14 ±1.94x10-14)	0.031±0.001	-	-	-	-
^{212}Bi	γ	-	-	-	-	-	-	-	-	-	-	(<2.9x10-13)	<0.15
^{208}Tl	γ	(7.62x10-25 ±1.52x10-25)	0.005±0.001	(9.14x10-25)	0.006±0	(25.9x10-25 ±7.62x10-25)	0.017±0.005	(44.2x10-25 ±3.04x10-25)	0.029±0.002	-	-	-	-

TABLE A3 LAMBTON GENERATING STATION

Analyte	Method	Coal		Bottom Ash		Fly Ash		Coal Pile R/O		Ash System O/F	
		(µg/g)	(Bq/g)	(µg/g)	(Bq/g)	(µg/g)	(Bq/g)	(µg/L)	(Bq/g)	(µg/L)	(Bq/L)
U	NAA	0.9±0.3	(1.1x10-2 ±0.4x10-2)	5.5±0.6	(6.8x10-2 ±0.8x10-2)	8.8±0.7	(10.8x10-2 ±0.8x10-2)	12±8	(14x10-2 ±10x10-2)	2.21±1.8	(2.7x10-2 ±2.2x10-2)
Th	NAA	1.6±0.3	(6.4x10-3 ±1.2x10-3)	12.8±1.6	(51.6x10-2 ±6.4x10-3)	19.3±1.7	(77.8x10-3 ±6.8x10-3)	29±29	(116x10-3 ±116x10-3)	<1	(<4x10-3)
U Series											
^{234}Th	Y	(1.28x10-11 ±1.40x10-11)	0.011±0.012	(5.13x10-11 ±3.15x10-11)	0.044±0.027	(9.09x10-11 ±5.48x10-11)	0.078±0.047	(<1.4x10-10)	<0.12	(<1.2x10-9)	<1
^{230}Th	α	(8.4x10-5 ±5.6x10-5)	0.06±0.04	(11x10-3 ±4.2x10-11)	0.008±0.03	(12.5x10-3 ±2.8x10-3)	0.09±0.02	(5.5x10-4 ±1.3x10-4)	0.39±0.09	(1.4x10-5 ±0.56x10-5)	0.01±0.004
^{226}Ra	Y	(35.5x10-7 ±0.546x10-7)	0.130±0.002	(15.6x10-7 ±1.64x10-7)	0.057±0.006	(24.6x10-7 ±4.64x10-7)	0.090±0.017	(<4.9x10-6)	<0.18	(<2.7x10-5)	<1
^{214}Pb	Y	(6.6x10-15 0.833x10-15)	0.008±0.001	(53.3x10-15 ±6.66x10-15)	0.064±0.008	(85.0x10-15 ±11.6x10-15)	0.102±0.014	(<1.3x10-13)	<0.18	(<2.5x10-13)	<0.3
^{214}Bi	Y	(4.84x10-15 ±0.606x10-15)	0.008±0.001	(38.2x10-15 ±4.24x10-15)	0.063±0.007	(62.4x10-15 ±7.27x10-15)	0.103±0.012	(<1.1x10-13)	<0.18	(<60x10-15)	<0.1
^{210}Pb	Y	-	-	-	-	-	-	-	-	(7x10-7)	2
Th Series											
^{232}Th	α	(2.5)	0.01	(12.4±2.5)	0.05±0.01	(14±2.5)	0.06±0.01	(60±32)	0.24±0.13	(<2.5)	<0.01
^{228}Th	α	(6.6x10-10 ±3.3x10-10)	0.02±0.01	(16x10-10 ±3.3x10-10)	0.03±0.01	(16x10-10)	0.05±0	(7.6x10-9 ±4.3x10-9)	0.23±0.13	(<3.3x10-10)	<0.01
^{212}Pb	Y	(9.68x10-14 ±1.94x10-14)	0.005±0.001	(85.2x10-14 ±19.4x10-14)	0.044±0.010	(134x10-14 1226x10-14)	0.069±0.117	-	-	-	-
^{212}Bi	Y	-	-	-	-	-	-	-	-	(<2.7x10-13)	<0.15
^{208}Tl	Y	(7.62x10-25 ±0.610x10-25)	0.003±0.0004	(62.5x10-25 ±6.10x10-25)	0.041±0.004	(110x10-25 ±16.8x10-25)	0.072±0.011	-	-	-	-

TABLE A4 BOUNDARY DAM GENERATING STATION

Analyte	Method	Coal		Bottom Ash		Fly Ash		Coal Pile R/O		Ash System O/F	
		(μg/g)	(Bq/g)	(μg/g)	(Bq/g)	(μg/g)	(Bq/g)	(μg/L)	(Bq/g)	(μg/L)	(Bq/L)
U	NAA	2.0±0.3	(2.4×10^{-2} $\pm0.4\times10^{-2}$)	12.7±3.1	(15.6×10^{-2} $\pm3.8\times10^{-2}$)	14.2±3.2	(17.4×10^{-2} $\pm3.9\times10^{-2}$)	93±152	(1.2±1.86)	5.8±1.1	(7.1×10^{-2})
Th	NAA	3.7±0.5	(15×10^{-3} $\pm2\times10^{-3}$)	22.7±5.0	(91.4×10^{-3} $\pm20\times10^{-3}$)	26.8±7.0	(100×10^{-3} $\pm28\times10^{-3}$)	360±573	(1.45±2.3)	<1	($<4\times10^{-3}$)
U Series											
^{234}Th	γ	(4.20×10^{-11} $\pm1.98\times10^{-11}$)	0.036±0.017	(8.16×10^{-11} $\pm5.36\times10^{-11}$)	0.070±0.046	(1.32×10^{-11} $\pm8.86\times10^{-11}$)	0.113±0.076	(1.64×10^{-10} $\pm4.5\times10^{-12}$)	0.14±0.004	($<1.2\times10^{-9}$)	<1
^{230}Th	α	(4.2×10^{-3})	0.03	(16×10^{-5} $\pm16\times10^{-5}$)	0.12±0.12	(20×10^{-5} $\pm9.7\times10^{-5}$)	0.15±0.07	(4.3×10^{-4})	0.32	(1.4×10^{-5} $\pm1.4\times10^{-5}$)	0.01±0.01
^{226}Ra	γ	(5.74×10^{-7} $\pm0.82\times10^{-7}$)	0.021±0.003	(49.5×10^{-7} $\pm3.28\times10^{-7}$)	0.181±0.012	-	-	(4.4×10^{-6} $\pm3.8\times10^{-6}$)	0.16±0.14	($<2.7\times10^{-5}$)	<1
^{214}Pb	γ	(16.6×10^{-15} $\pm1.66\times10^{-15}$)	0.020±0.002	(106×10^{-15} $\pm15.8\times10^{-15}$)	0.127±0.019	(160×10^{-15} $\pm8.33\times10^{-15}$)	0.193±0.010	($<1.5\times10^{-13}$)	<0.18	($<2.5\times10^{-13}$)	<0.3
^{214}Bi	γ	(11.5×10^{-15} $\pm0.606\times10^{-15}$)	0.019±0.001	(77.0×10^{-15} $\pm10.9\times10^{-15}$)	0.127±0.018	(110×10^{-15} $\pm3.03\times10^{-15}$)	0.181±0.005	(1.0×10^{-13} $\pm5.5\times10^{-14}$)	0.17±0.09	($<60\times10^{-15}$)	<0.1
^{210}Pb	γ	-	-	-	-	-	-	-	-	($<7\times10^{-7}$)	<2
Th Series											
^{232}Th	α	(5.0)	0.02	(18±7.4)	0.07±0.03	1.8±9.9	0.07±0.04	(774)	3.0	(<2.5)	<0.01
^{228}TH	α	(6.6×10^{-10})	0.02	(23×10^{-10} $\pm13\times10^{-10}$)	0.07±0.04	(26×10^{-10} $\pm13\times10^{-10}$)	0.08±0.04	(9.9×10^{-8})	3.0	(3.3×10^{-10} $\pm1.32\times10^{-10}$)	0.01±0.004
^{212}Pb	γ	(21.3×10^{-10} $\pm1.94\times10^{-14}$)	0.011±0.001	(136×10^{-14} $\pm17.4\times10^{-14}$)	0.070±0.009	(217×10^{-14} $\pm34.8\times10^{-14}$)	0.112±0.018	-	-	-	-
^{212}Bi	γ	-	-	-	-	-	-	-	-	($<2.7\times10^{-13}$)	<0.15
^{208}Tl	γ	(16.8×10^{-25} $\pm1.52\times10^{-25}$)	0.011±0.001	(111×10^{-25} $\pm16.8\times10^{-25}$)	0.073±0.011	(166×10^{-25} $\pm2.14\times10^{-25}$)	0.109±0.006	-	-	-	-

TABLE A5 SUNDANCE GENERATING STATION

Analyte	Method	Coal		Bottom Ash		Fly Ash		Coal Pile R/O		Ash System O/F	
		(μg/g)	(Bq/g)	(μg/g)	(Bq/g)	(μg/g)	(Bq/g)	(μg/L)	(Bq/g)	(μg/L)	(Bq/L)
U	NAA	2.3±0.6	(2.8x10-2 ±0.8x10-2)	11.3±6.2	(13.8x10-2 ±7.6x10-2)	12.3±2.1	(15.1x10-2 ±2.6x10-2)	46±41	(0.56±0.50)	7.9±4.4	(9.7x10-2 ±5.4x10-2)
Th	NAA	4.0±0.6	(16x10-3 ±2x10-3)	19.4±3.2	(78.2x10-3 ±12.8x10-3)	24.3±3.1	97.9x10-3 ±12.4x10-3)	212±150	(0.85±0.60)	13.6±11.7	(54.8x10-3 ±47.2x10-3)
U Series											
^{234}Th	γ	(3.85x10-11 ±1.75x10-11)	0.033±0.015	12.4x10-11 ±11.5x10-11)	0.106±0.099	(17.0x10-11 ±8.86x10-11)	0.146±0.076	(5.4x10-10 ±5.8x10-10)	0.46±0.50	(<1.2x10-9)	<1
^{230}Th	α	(9.8x10-5 ±1.4x10-5)	0.07±0.01	(25x10-5 ±5.6x10-5)	0.18±0.04	(11x10-5 ±5.6x10-5)	0.08±0.04	(2.7x10-3 ±2.0x10-3)	1.94±1.43	(4.60x10-5 ±5.43x10-5)	0.033±0.039
^{226}Ra	γ	(5.19x10-7 ±1.37x10-7)	0.019±0.005	(26.0x10-7 ±7.65x10-7)	0.095±0.028	(41.0x10-7 ±7.10x10-7)	0.150±0.026	(1.6x10-5 ±.2x10-5)	0.58±0.44	(<2.7x10-5)	<1
^{214}Pb	γ	(14.2x10-5 ±1.66x10-15)	0.017±0.002	(95.8x10-15 ±15.0x10-15)	0.115±0.18	(132x10-15 ±14.2x10-15)	0.159±0.017	(52x10-13 ±2.9x10-13)	0.62±0.035	(<2.5x10-13)	<0.3
^{214}Bi	γ	(10.3x10-15 ±1.82x10-15)	0.017±0.003	(72.7x10-15 ±7.27x10-15)	0.120±0.012	(92.7x10-15 ±9.70x10-15)	0.153±0.016	(3.8x10-13 ±2.1x10-13)	0.63±0.34	(<60x10-15)	<0.1
^{210}Pb	γ	-	-	-	-	-	-	-	-	(<7x10-7)	<2
Th Series											
^{232}Th	α	(5.0)	0.02	(24±5.0)	0.10±0.02	(18±2.4)	0.07±0.01	(231±37)	0.93±0.15	(4.47±4.47)	0.018±0.018
^{228}TH	α	(6.6x10-10 ±3.3x10-10)	0.02±0.01	(36x10-10 ±13x10-10)	0.11±0.04	(26x10-10)	0.08	(3.1x10-8 ±3.0x10-9)	0.94±0.15	(2.64x10-10 ±1.32x10-10)	0.008±0.004
^{212}Pb	γ	(21.3x10-14 ±3.88x10-14)	0.011±0.002	(143x10-14 ±19.4x10-14)	0.074±0.010	(162x10-14 ±21.3x10-14)	0.084±0.011	-	-	-	-
^{212}Bi	γ	-	-	-	-	-	-	-	-	(<2.7x10-13)	<0.15
^{208}Tl	γ	(16.8x10-25 ±3.04x10-25)	0.011±0.002	(117x10-25 ±15.2x10-25)	0.077±0.010	(162x10-25 ±16.8x10-25)	0.09±011	-	-	-	-

TABLE A6 MILNER GENERATING STATION

Analyte	Method	Coal		Bottom Ash		Fly Ash		Coal Pile R/O		Ash System O/F	
		(µg/g)	(Bq/g)	(µg/g)	(Bq/g)	(µg/g)	(Bq/g)	(µg/L)	(Bq/g)	(µg/L)	(Bq/L)
U	NAA	3.9±0.8	(4.8×10^{-2} ±1×10^{-2})	6.7±1.1	(8.2×10^{-2} ±1.0×10^{-2})	8.4±3.1	(10×10^{-2} ±3.8×10^{-2})	54±12	(0.66±0.14)	7±5	(8×10^{-2} ±6×10^{-2})
Th	NAA	6.5±1.6	(20×10^{-3} ±6.4×10^{-3})	11.9±1.7	(48.0×10^{-3} ±6.8×10^{-3})	13.8±4.8	(0.056×10^{-3} ±20×10^{-3})	192±56	(0.77±0.22)	11±11	(44×10^{-3} ±44×10^{-3})
U Series											
^{234}Th	γ	(4.55×10^{-11} ±3.73×10^{-11})	0.039±0.032	(14.8×10^{-11} ±7.81×10^{-11})	0.127±0.067	(13.4×10^{-11} ±11.0×10^{-11})	0.115±0.094	(8.2×10^{-10} ±6.6×10^{-10})	0.70±0.56	(<1.2×10^{-9})	<1
^{230}Th	α	(9.7×10^{-5} ±1.4×10^{-5})	0.07±0.01	(9.7×10^{-5} ±7.0×10^{-5})	0.07±0.05	(20×10^{-5} ±9.7×10^{-5})	0.15±0.07	(1.8×10^{-3} ±1.5×10^{-3})	1.32±1.1	(5.6×10^{-5} ±1.4×10^{-5})	0.04±0.01
^{226}Ra	γ	(9.02×10^{-7} ±1.64×10^{-7})	0.033±0.006	(23.2×10^{-7} ±4.64×10^{-7})	0.085±0.017	(30.9×10^{-7} ±6.56×10^{-7})	0.113±0.024	(2.6×10^{-5} ±1.2×10^{-5})	0.96±0.62	(<2.7×10^{-5})	<1
^{214}Pb	γ	(25.0×10^{-15} ±3.33×10^{-15})	0.030±0.004	(70.8×10^{-15} ±6.66×10^{-15})	0.085±0.008	(106×10^{-15} ±15.0×10^{-15})	0.128±0.018	(5.6×10^{-13} ±3.7×10^{-13})	0.67±0.44	(<2.5×10^{-13})	<0.3
^{214}Bi	γ	(18.2×10^{-15} ±1.82×10^{-15})	0.030±0.003	(51.5×10^{-15} ±4.24×10^{-15})	0.085±0.007	(77.0×10^{-15} ±9.70×10^{-15})	0.127±0.016	(5.0×10^{-13} ±2.2×10^{-13})	0.82±0.36	(<60×10^{-15})	<0.1
^{210}Pb	γ	-	-	-	-	-	-	-	-	(<7×10^{-7})	2
Th Series											
^{232}Th	α	(9.9)	0.04	(12±9.9)	0.05±0.04	(14±9.9)	0.06±0.04	(146±27)	0.59±0.11	(7.4±2.5)	0.03±0.01
^{228}TH	α	(16×10^{-10} ±3.3×10^{-10})	0.05±0.01	(20×10^{-10} ±16×10^{-10})	0.06±0.05	(20×10^{-10} ±13×10^{-10})	0.06±0.04	(2.1×10^{-8} ±7.3×10^{-9})	0.65±0.22	(9.9×10^{-10} ±3.3×10^{-10})	0.03±0.01
^{212}Pb	γ	(32.9×10^{-16} ±1.94×10^{-14})	0.017±0.001	(93.0×10^{-14} ±7.75×10^{-14})	0.048±0.004	(132×10^{-14} ±17.4×10^{-14})	0.068±0.009	-	-	-	-
^{212}Bi	γ	-	-	-	-	-	-	-	-	-	-
^{208}Tl	γ	(25.9×10^{-25} ±4.57×10^{-25})	0.017±0.003	(73.2×10^{-25} ±6.10×10^{-25})	0.048±0.004	(97.6×10^{-25} ±25.9×10^{-25})	0.064±0.017	-	-	(<2.7×10^{-13})	<0.15
								-	-	-	-

TABLE A7 CONVERSIONS FROM CONCENTRATION TO ACTIVITY

Radionuclide	Conversion Factor µg/Bq
^{238}U	1.23×10^{-2}
^{232}Th	4.03×10^{-3}
^{234}Th	1.17×10^{-9}
^{230}Th	1.40×10^{-3}
^{226}Ra	2.73×10^{-5}
^{210}Pb	3.33×10^{-7}
^{232}Th	248
^{228}Th	3.30×10^{-8}
^{214}Pb	8.33×10^{-13}
^{214}Bi	6.06×10^{-13}
^{212}Pb	1.94×10^{-11}
^{212}Bi	1.83×10^{-12}
^{212}Po	1.52×10^{-22}